Recent bioreduction of hexavalent chromium in wastewater treatment: A review

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ABSTRACT

Hexavalent chromium (Cr(VI)) in water is a proven carcinogen to different internal and external organs of the living organisms. There are different human activities incorporated to the anthropogenic sources in the environment enriching Cr(VI) of high concentration in the water system above the regulatory level. The physical, chemical and biological properties of chromium favour the dissolution in the water environment. This concerns the environmental researcher to tackle and mitigate. Chemical or biological techniques or a combination of the two have been used to remove Cr(VI) from polluted waters. Biological techniques include integrated bioremediation, such as the primary processes of direct bioreduction and biosorption, and secondary processes of microbial fuel cell, biostimulation, surface modified dry biomass and biochar adsorption, and engineered biofilm and cell free reductase. These techniques are used by a wide range of living organisms including bacteria, fungi, plants, plant leaves, plant nuts and algae. This group of living organisms transform and remove Cr(VI) from water during the cellular metabolisms, extracellular activities, physical and chemical adsorptions on the cell surface, and photosynthesis. Variation of different physical, chemical and environmental parameters affecting the efficiency of the bioremediation process have impacted on the design of bioreactors. There has been a recent development of a microbial fuel cell which use the proximity of Cr(VI) reduction as a cathode half cell for the generation of renewable energy and simulation of its' removal from water.

Kewwords: Hexavalent chromium; Wastewater treatment; Toxicity; Bioreduction mechanism; Bioremediation

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1. Introduction

Environmental pollutants can be widely dispersed in the biosphere from pond to ocean, grassland to mountain, troposphere to exosphere, natural to built-up ecosystem [1,2]. Pollutants can cause drastic changes in the physical, chemical and mechanical properties of the abiotic components resulting in numerous changes to the biodiversity. This concerns sustainable development of pollution control found almost in every scientific, social, or political agenda all over the world. Many developed and developing countries are implementing new regulations or amendments to old regulations for prevention, control and abatement of the environmental pollutions [3,4]. Also many countries are executing different missions, awareness programs and workshops in the socio-economical forums. Worldwide, many researchers are working to tackle and mitigate the effects of the various environmental pollutions.

Pollution of water is a major environmental problem resulting from the hydrological cycle. There are many non-degradable, toxic or otherwise harmful chemicals produced by a variety of different sources such as manufacturing industries and other human activities that contaminate water supplies [5]. Hexavalent chromium Cr(VI) is an important water pollutant. Even at Cr(VI) levels measuring in the parts per billion (ppb), research has shown it to be toxic. [6] Cr(VI) can originate from different anthropogenic activities such as chromite mining, leather tanning, pigment synthesis, electroplating and metal finishing.

Heavy metals such as barium, beryllium, cadmium, mercury, lead, chromium, arsenic, copper, selenium, antimony and thallium all cause toxicity in water depending on their concentration. [3,4] The National Primary Drinking Water Regulations of United States Environmental Protection Agency for heavy metals are given in table 1. With the exception of chromium, the toxicity of other heavy metals is accounted by their total concentration irrespective of the oxidation state in the aqueous medium. Chromium is unique among regulated toxic elements in the environment as different chromium species exist, specifically chromium (III) and chromium (VI). [6] Chromium is found in the environment in its natural form as Cr(III). However, generation of Cr(VI) is created by the oxidation of Cr(III) during various industrial processes and is discarded as industrial wastes. The properties of Cr(VI) are so favorable that it becomes a 'guest' for many physical and chemical components in the environment. Transportation of Cr(VI) within the terrestrial and aquatic environments is greatly affected by chemical speciation. The affinity to chemical and photochemical redox transformations, precipitation, dissolution, adsorption and desorption processes occurring in individual trophic level of the environment determines the biogeochemical cycle of Cr(VI) as shown in figure 1 [7]. Cr(VI) is ultimately consumed by different plant and animal life of the environment. This can cause serious health problem. For example, Cr(VI) acts

as an oxidant directly to the surface of skin or absorption can occur through the skin, especially if the skin surface is damaged. Chromium absorbed into the blood system via the lungs is excreted by the kidney and liver. Prolonged absorption causes acute kidney and liver damage due to severe inflammation inside the cells [6,8].

If Cr(VI) concentrations in the abiotic components of the ecosystem increase above the regulatory standards, stringent legislation for the prevention, control and protection of the environment needs to be considered [3,4].

Environmental concentration of chromium is known to increase due to the industrial developments. Three forms of chromium such as Cr(0), Cr(III) and Cr(VI) are present in the soil, water and biota. Different species of chromium originate from different anthropogenic sources such as chrome alloy production in steel industries, chrome electroplating, airborne emissions from chemical plants and incineration facilities, cement dust, contaminated landfill, effluents from chemical plants, asbestos lining erosion, road dust from catalytic converter erosion and asbestos brakes, tobacco smoke, topsoil and rocks, copier servicing, anti-algae agents, antifreeze, cement, glassmaking and leather tanning. [9, 10] In the industrial processes, chromium extraction begins with mining of chromite ores (Cr_2O_3) or ferrous chromite ($FeO.Cr_2O_3$). These ores are converted to metallic chromium via various stages and processes of oxidation and reduction. [7] There are some direct uses of chromite ores, most notably for the production of refractory bricks. [11] About 90% of total chromite ores are consumed as an alloying agent in the form of ferrochromium to produce either stainless steel or used in other nonferrous metallurgical industries. The remaining 10 % of chromite ores are used in refractory, cement, glass, ceramic, machinery, leather tanning, electroplating, wood preservation, and pigment industries. [10] World stainless steel producers depend directly or indirectly on chromium supply. According to the mineral commodity

summaries 2016 by the US Geological Survey, the total world reserve of shipping grade chromite ore is estimated to be more than 480 × 10^6 metric tons. [12] Kazakhstan has approximately 50% of world shipping grade chromite ore but South Africa is top for mining ferrous chromite for the last two years. China has emerged as the top stainless steel producer and is the leading chromium-consuming and ferrochromium-producing country. About 95% of the world's chromium resources are geographically concentrated in Kazakhstan and southern Africa. The details data is given in table 2.

Possibility of Cr(VI) pollution is not surprising due to its chemical compatibility to the environment and wide range of industrial applications. Hence its removal is obvious because of the toxicity effects on the human body. Cr(VI) removal is gaining importance in the environmental research communities worldwide. Every year numbers of research article have been reported experimenting different techniques. Several review articles have been reported so far summarizing the Cr(VI) toxicity and removal. [6-10, 13, 19, 44, 48] The major reviews deal with the genotoxicity of Cr(VI) on human body. Very few reviews deal with Cr(VI) removal with an emphasison soil pollution rather than water pollution. Every year new techniques have been discovered to remove Cr(VI) from water, we have attempted to review the bioreduction of Cr(VI) on the basis of the recent interventions. In addition to the previous reviews, this review gives more data towards the bioreduction of Cr(VI). We have summarized more than hundred new isolated species from different locations enabling Cr(VI) tolerance and removal capacity. Some of them are listed in a table form (Table 5).

2. Chemistry of Chromium Causing Contaminations

Chromium is a d-Block transition elements and first member of the group 6 of the modern periodic table. Since the ground state electronic configuration of chromium is 'high spin' $[Ar]4s^1 3d^5$, it shows varying oxidation states such as -2, -1, 0, +1, +2, +3, +4, +5 and +6 with an associated wide range of chemical and physical properties. [13] It can form acidic, alkaline or amphoteric oxides according to the oxidation state. The most stable chromium occurs when the oxidation states are +3 (trivalent, Cr(III)) and +6 (hexavalent, Cr(VI)). In the water most Cr(VI) species are $Cr_2O_7^{2-}$, CrO_4^{2-}, H_2CrO_4, and $HCrO_4^-$. Similarly, Cr(III) species in solution are most often Cr^{3+}, $Cr(OH)_2^+$, CrO^+, $HCrO_2$ and CrO_2^-. [8] Chromium metal is a steely-grey colour, has a metallic luster, is hard and brittle, resists tarnishing, and has high melting and boiling points (1,907 ºC and 2,671 ºC respectively). [13,14] Chromium metal is passivated by oxidation reactions and this forms a thin protective surface layer which prevents the diffusion of oxygen onto the underlying metal. Chromium metal shows a BCC crystal system similar to α-iron making it competent in stainless steel alloy. These properties make chromium a suitable element to improving alloys and increase corrosion resistivity, change the colour, metallic lusture and/or hardness [15]. Cr(VI) is an environmental leachate of stainless steel fabrication, which contributes to pollution of Cr(VI) in water and soils. Due to its high melting point, chromium is added to manufacture refractory bricks and is used in glass and ceramic industries. Chromium metal in refractory bricks is oxidized to Cr(VI) during the high temperature refractory manufacturing process and can contaminate soil and water due to leaching.

Cr(VI), as Na_2CrO_4, is produced during the lime treatment of chromite or ferrous-chromite ores resulting in further compounds or ions being formed such as CrO_3, CrF_6, $CrOCl_4$, $H_2Cr_2O_7$,$Cr_2O_7^{2-}$, CrO_4^{2-}, H_2CrO_4, and $HCrO_4^-$ [16]. These are highly soluble in water and show strong oxidizing potential. For redox titration Cr(VI) in the form of sodium dichromate ($Na_2Cr_2O_7$) or potassium

dichromate ($K_2Cr_2O_7$) used as oxidizing standards, however, $K_2Cr_2O_7$ is preferable due to the hygroscopic nature of $Na_2Cr_2O_7$. Usually Cr(VI) does not favor complex formation, but, in presence of hydrogen peroxide it forms peroxo species which capable of forming coordination complexes. In different manufacturing industries, such as the production of dyes and paint pigments, lather tanning, analytical grade chemicals, electroplating, and others, $H_2Cr_2O_7$ is used. The effluents from these industries are the one of the major reasons for Cr(VI) contamination in the hydrosphere [6].

In contrary trivalent chromium Cr(III) is very stable in an acidic environment and easily oxidized to Cr(VI) in an alkaline medium. Cr(III) compounds form numerous octahedral coordination complexes. The stability is determined by the crystal field stabilization energy from its d^3 configuration. Cr(III) complexes show different colours due to different crystal field transitions in presence of coordinating ligands. The solubility of Cr(III) compounds is less compared to Cr(VI) in aqueous medium.. [10]. Below pH 5.0 oxides of Cr(III) are slightly soluble in water but above pH 5.0 Cr(III) forms hydrated compounds which are even less soluble. However, Cr(VI) predominantly forms anionic species in water increasing the solubility to above 60 g/L at a wide range of temperatures. The thermodynamic Eh-pH diagram (Pourbaix Diagram, figure 2) shows the stability of Cr(III) and Cr(VI) and pH is an important parameter for the redox chemistry of chromium. The high Eh values prefers oxidizing species and vice versa. In strong acidic conditions (pH<1) and at high Eh, Cr(VI) exists as chromic acid (H_2CrO_4) which is a strong oxidizing agent. Between pH 1.0 and 6.0, anionic species $HCrO_4^-$ is stable at a high Eh. With decreasing Eh, equilibriums of $HCrO_4^-$ exist with Cr(III) from pH 1.0 to 4.0 and with $Cr(OH)_2^+$ from pH 4.0 to 6.0. Above pH 6.0 Cr(VI) exists as CrO_4^{2-} and with decreasing Eh the equilibriums exist with Cr(III) as CrO^+ (pH 6.0 to 8.0), $HCrO_2$ (pH 8.0 to 9.5) and CrO_2^- (pH 9.5 to 14.0). Since the

solubility of Cr(VI) species is very high at all range of pH, its removal from water is possible by reducing the species to the less soluble Cr(III). This can be followed by hydration to solidify the reduced species rather than by direct precipitation of Cr(VI). The adsorption process showed attachment of the anionic species of Cr(VI) on the polar functional surface in the acidic medium [17]. The hypothetical mechanism of adsorption Cr(VI) may be as follow accordingly shown in equation 1.

Functional surface + H^+ + CrO_4^{2-}

$$\rightarrow \text{(Functional surface-H)}^+\ldots(CrO_4)^{2-}\ldots{}^+\text{(H-Functional surface)} \qquad (1)$$

3. Toxicity of Chromium

Cr(III) is an essential trace element necessary for glucose, lipid and amino acid metabolism. It is a popular dietary supplement seen in table 3. Chromium is found in different parts of human body as listed in table 4. Chromium occurs in the tissues of human fetuses and infants. From birth its content continues to decrease with increasing age in all body organs except the lungs, in which a slight rise in chromium content is detectable from the 10th year of life, apparently as a consequence of inhaled chromium deposits in the lungs. The highest accumulation of chromium (0.234-3.8 mg/kg) was found in the hair. However, at high concentration, Cr(III) causes negative effects on cellular structures. Evidence is growing that metabolites of Cr(III) dietary supplements are partially oxidized to carcinogenic Cr(VI), Cr(IV) and Cr(V) in vivo by intracellular oxidation. [18] Cr(VI) forms anionic species CrO_4^{2-} in solution within pH 6.0 as shown in figure 2. The structure of this anionic species is similar to the sulphate ion (SO_4^{2-}). The CrO_4^{2-} ion can substitute the SO_4^{2-} and be transported via the sulphate transport system and enters in to the cells. [19] As Cr(VI) is a

strong oxidizer and, when combined with different reducing agents inside the cells, forms intermediates of Cr(V) and Cr(IV) before conversion to Cr(III) as an end product. During the reduction of Cr(VI) to Cr(III) the formation of different reactive species like nascent oxygen(O), superoxide ions (O_2^-), hydroxyl ions (OH^-), peroxo ions (O_2H^-) and free radicals are catalyzed inside the cells. [8] The intracellular generations of the reactive species depend on Cr(VI) concentration as free radical generation increases with greater chromium exposure. [20] Cellular metabolism of Cr(VI) can cause both oxidative and non-oxidative forms of DNA damage. The most abundant and specific type of DNA damage is Cr-DNA binding (adducts). This has been detected in reduction reactions in vitro and in various cultured cells which cause mutations and chromosomal breaks [19]. The reactive species produced during the intracellular Cr(VI) reduction combined with DNA-proteins to forms different intermediate products called oxidative DNA damage. The electrostatic interaction between stable Cr(III) species and negatively charged phosphate groups of DNA forms mutagenic and toxic Cr(III)–DNA complexes. These complexes affect the natural DNA replication and transcription and can cause mutagenesis. In addition to the formation of metal complexes, Cr(VI) metabolism has been associated with the production of DNA single-strand breaks [21]. These can alter the function of cells leading to cancers in the liver, kidney and lungs developing. Similarly, different passivation takes place through the skin on direct contact of Cr(VI), causing dermatitis, dermal necrosis and dermal corrosion. [6] Occupational exposures to Cr(VI) via inhalation have consistently been found to increase the risk of cancers in the respiratory system [22]. Both highly and poorly soluble chromates were determined to be carcinogenic [23]. Long-term occupational exposure to Cr(VI) from different chromate industries and chromite mines is a chemical carcinogen that can cause carcinomas of the bronchial systems. Zhang and Li [24] reported increased mortality from stomach cancers among rural residents in the

Liaoning Province of China where drinking water was heavily contaminated with Cr(VI) released by the ore smelting facility. Cr(VI) has shown neurotoxicity by significantly reducing the number of neuronal cells [25]. Cr(VI) develops physiological stress in animals by damaging sperm and male reproductive systems [26].

4. Chromium Reduction

4.1 Comparison of conventional and bioremediation methods

Hexavalent chromium can be reduced by different conventional physico-chemical processes. This is important to environmental researchers because of the toxicity effects on the human body. Recent developments in the understanding of the conventional process emphasize various methods such as thermal treatment [27], desalination [28], direct reduction [29,30], resin adsorption [31,32,214,217], electrolysis [33,34], electrocoagulation [35,36], activated carbon adsorption [212, 213], composite ceramic adsorption [37, 215, 218], carbon nano fibers adsorption [211, 216], nano materials catalyzed reduction [38,39], and catalytic reduction [40,41]. The conventional processes are complex due to the different intensive sub-processes and use of large amounts of chemicals and generation of toxic sludges. [13,42,43] Carbothermal reduction of Cr(VI) was conducted by adding carbon at temperature ranging from 1000 to 1400ºC in a TGA apparatus with particle size limitation of the Cr(VI) contaminated soil sample [27]. To achieve a complete reduction 15% carbon was added to soil, however, evaluation of CO_2 emission was ignored during the process. A complex electrochemical desalination method used to reduce Cr(VI). [28] In the process two costly membranes were used to separate the desalination chamber from anode and cathode [28]. Similarly in the other conventional methods, stringent chemical environments were

employed in the complex designed reactors to reduce/adsorb the Cr(VI). Synthesis of different nano materials, carbon fibers, composites, costly resins were used in the conventional methods for the reduction/adsorption of Cr(VI) making the process more complicated in terms of cost evaluation and eco-friendliness. [28-43, 211-218] The in-situ reduction of Cr(VI) from water does not favour the conventional process as it has multiples steps to set up the pilot scale operation at the location of the pollution. When considering all the demerits of the conventional methods, the focus has been shifted to better alternative treatment methods. Biological detoxification of Cr(VI) to relatively less toxic and less mobile Cr(III) is likely to be a useful process for the remediation of contaminated waters and soils compared to the chemical processes [44,45]. The biological processes occur in natural cellular metabolisms of the biological species remediating Cr(VI) from different resources. The details of the biological reduction mechanism are discussed in the following section. From the mechanism, the reasons why the biological method are superior to the conventional processes can be elucidated. This has stimulated the interest in microorganisms that can use Cr(VI) as an electron acceptor. The biological detoxification involves different inner and outer cellular reactions such as direct reduction by chromium reducing bacteria, biosorption, and phytoremediation, and indirect reduction by application of different electron shuttles, bioremediation, and bioaccumulation [13,46]. The ascorbate with glutathione and cysteine produced during the cellular metabolism is responsible for more than 95% of Cr(VI) reduction [49,50]. The natural biological process do not need any complex designing as it involves a simple metabolism process. In this case, no need of raising temperature as the biological species grow at the ambient atmospheric conditions. Usually the biological species used in the bioreduction process are indigenous species do not need any extra nutrient for their growth when they are used in the scale up applications [43]. The bioremediation processes are usually single step process and

rarely do they undergo multiple steps enabling implementation more convenient. All together the bioremediation emerges as a superior to conventional processes.

4.2 Biological reduction mechanism

Hexavalent chromium develops intracellular toxicity through a variety of mechanisms including reduction of Cr(VI) to Cr(III), generation of reactive species, Cr-DNA complex formation, protein denaturation and electrostatic interactions [19,47]. Despite numerous toxicity effects, there are different microbes which have shown a tolerance to Cr(VI) with concentrations above the standard regulation level. Chromium tolerance has been described in terms of cellular accumulation, extracellular reduction, adsorption, intracellular reduction followed by salt liberation, counter enzyme system and efflux mechanisms [48]. Biological systems lack the ability to re-oxidize Cr(III) to Cr(VI). Extracellular reduction of Cr(VI) is a detoxification process that produces nontoxic Cr(III) which is unable to pass through the cell membranes. Studies of reduction activities in tissue homogenates and biological fluids showed that ascorbate was the principal biological reducer of Cr(VI), accounting for 80-95% of its metabolism [49]. A combined activity of ascorbate with glutathione and cysteine is responsible for >95% of Cr(VI) reduction in vivo. The concentrations of glutathione and ascorbate in the tissues are not usually different, and the predominant role of ascorbate stems from its very high rate of Cr(VI) reduction. [50] Depending on the nature of the reducing agent, its concentration, and stoichiometry, Cr(VI) reduction reactions generate variable amounts of transient products such as Cr(V), Cr(IV), and sulfur- and carbon- based radicals. [51] As expected for these important biological antioxidants, glutathione,

cysteine and ascorbate derived radicals formed in Cr(VI) reactions are unreactive toward DNA. [52]

Both soluble and membrane-associated enzymes have mediated the process of Cr(VI) reduction under anaerobic conditions. Cytochromes b and c present in the cells are involved in the transportation of an electron within the cells resulting in enzymatic anaerobic Cr(VI) reduction. [53] Under anaerobic conditions, Cr(VI) serves as a terminal electron acceptor in the membrane electron-transport respiratory pathway. This process results in energy conservation for growth and cell maintenance where NADH, carbohydrates, proteins, fats, hydrogen, and endogenous electron reserves donate electrons to Cr(VI). [54] In the aerobic reaction, the Cr(VI) associates with oxygen and is the sole electron donor system forming different reactive oxygen species within the cell. This formation of reactive oxygen species catalyzes the Cr(VI) reduction with formation of series of different intermediate of Cr(IV) and Cr(V) until finally reduced to Cr(III). [55] This mechanism is shown in figure 3.

Indirect chromium reduction occurs in some iron and sulfur reducing bacteria. These groups of microbes produce different metabolites such as Fe(II) or hydrogen sulphide (H_2S). The reduction of Cr(VI) by H_2S involves three stages: (a) reduction of sulfates, (b) reduction of chromate by sulfides and (c) precipitation of Cr(VI) by sulfide. [56] The reduction of Cr(VI) by Fe(II) occurs when iron reducing bacteria reduces Fe(III) to Fe(II), which in turn reduces Cr(VI) to Cr(III). The kinetics of the indirect reduction of chromium in iron and sulfur reducing bacteria is greater than that of direct biological chromium reduction. [57] Once the Cr(VI) has been reduced to Cr(III), it accumulates in cells by the formation of coordination complexes with proteins. There are many electron rich proteins produced by microbes in both the intracellular and extracellular

environments. Cr(III) favourably forms chelating complexes with proteins, which is the major reason for accumulation of Cr(III). [58]

Efflux mechanism for chromium resistance bacteria are described by formation of hydrophobic protein *ChrA* a product of *chrA* gene. Chromate tolerance conferred by the *ChrA* protein was associated with reduced accumulation of CrO_4^{2-} in both *P. aeruginosa* and *A. eutrophus*. [59] It was hypothesized by Alvarez et al.[59] that *ChrA* was involved in the extrusion of chromate ions. Branco et al.[60] reported that the highly tolerant strain *Ochrobactrum tritici* survived chromate concentrations above 50 mM and have the transposon Tn*OtChr*, which contains a group of *ChrB, ChrA, ChrC* and *ChrF* genes. The genes *ChrB* and *ChrA* genes were essential for establishing high resistance in chromium-sensitive *O. tritici*. They also reported that the *Chr* promoter was strongly induced by chromate or dichromate but was completely unresponsive to Cr(III), oxidants, sulfate, or other oxyanions. Induction of the *Chr* operon suppressed accumulation of cellular chromium through the activity of a chromate efflux pump that is encoded by *ChrA* [60].

Microbial heavy metal biosorption comprises of two phases: an initial rapid phase involving physical adsorption or ion exchange at cell surface and a subsequent slower phase involving active metabolism-dependent transport of heavy metal into the bacterial cells. During bioaccumulation, intracellular sequestration occurs followed by localization within specific organelles, metallothionein binding, particulate metal accumulation, extracellular precipitation and complex formation. [61,62] Biosorption is established as the mechanism of the challenging process to remove pollutants from aqueous medium. Saha and Orvig in 2010 [63] proposed four biosorption mechanisms of chromium; (a) anionic adsorption to cationic functional groups, (b) adsorption-coupled reduction, (c) anionic and cationic adsorption, and (d) reduction and anionic adsorption. Despite the fact that the mechanisms of metal binding by individual cellular organelles and

chemical moieties are known, sorption of metals to intact cells and cellular products such as biofilms is governed by a multiplicity of mechanisms and interactions, which are not always fully understood [64].

The cellular phenomena such as cellular accumulation, extracellular reduction, adsorption, intracellular reduction followed by salt liberation, counter enzyme system and efflux mechanisms showed compatibility of direct and indirect bioreduction. [48] The inherent properties of the biomass capable of performing the removal of Cr(VI) from the water system have been described in the mechanism above. Since biological processes are natural and eco-friendly, the environmental impact assessment has minimum role in the implementation in the pilot scale. Extensive researches are required to standardize the process along with evaluation of its feasibility for implementation in a cost-effective way.

5. Bioreduction of Cr(VI)

5.1 Bacteria

Microbial Cr(VI) reduction was first reported in the late 1970s. [65] The authors observed a Cr(VI) reduction capability in *Pseudomonas* species grown under anaerobic conditions. The active bacterial strain, isolated from sewage sludge, was classified as *Pseudomonas dechromaticans*. Since then a variety of microorganisms have been identified and isolated from a diverse range of environments with the capacity to remove Cr(VI) contamination. Several researchers have isolated microorganisms that catalyze the reduction of Cr (VI) to Cr(III) under various conditions and experimental design including changes to pH, temperature, degree of agitation, aerobic and anaerobically, initial Cr(VI) concentration, nutrient supplementation, cell free Cr(VI) reductase,

electron shuttle addition, changes to reactor design, cell immobilizers among others. [6,8,10] Bacteria endowed with the capacity to reduce Cr(VI) levels are named chromium-reducing bacteria (CRB). [66] CRB are generally isolated from industrial effluents, especially those from chromite mines [67], tanneries [68-70], textile industries [71], and electroplating manufacturing [72]. CRB have been isolated from soils contaminated with these effluents. [73-75] A list of isolates presented in table 5 for the reduction of Cr(VI) from deferent sources with briefly summarized processes.

Leucobacter sp. is a new finding isolated from a chromate-contaminated soil. The *Leucobacter* sp. showed a distinct and effective Cr(VI) reduction under aerobic growth conditions, followed by facultative anaerobic incubation for Cr(VI) reduction. [76] Ten Gram-negative bacteria isolated from a chromium contaminated effluent of industrial landfill were inoculated into Luria Bertani (LB) culture medium containing 100 mg/L Cr(VI). But only two bacteria *Alcaligenes faecalis* and *Pseudochrobactrum saccharolyticum* showed growth capacity within 48 h of incubation with minimum inhibitory concentrations (MIC) to Cr(VI) were above 100 mg/L. [77] The experiments were conducted with synthetic $K_2Cr_2O_7$ solution in LB media as well as industrial effluents without LB media at two sets of Cr(VI) concentration such as 10 and 100 mg/L. In the culture medium containing 10mg/L Cr(VI) concentration, 100% chromium removal was achieved in 48 h for both the isolates. *A. faecalis* showed an easy log phase after inoculation compared to *P. saccharolyticum*. At Cr(VI) concentrations of 100 mg/L, *A. faecalis* reduced 70% of Cr(VI) in 120 h of incubation with a log phase from 24 to 48 h. In the same medium, *P. saccharolyticum* achieved high cell concentration after 48 h of incubation but did not reduce Cr(VI) further. *P. saccharolyticum* reduced only 45% during incubation period of 72 to 120 h. Both the isolates showed 24 h as lag period in culture medium of 100 mg/L Cr(VI). In the industrial effluent without

additional nutrients, no reduction was observed for the either isolates. When nutrients in the form of carbon, nitrogen, and phosphorous were added to the effluent, both the isolates showed complete reduction of Cr(VI) in 72 h of incubation. This implied that nutrients are a limiting factor for the reduction of Cr(VI). These nutrients worked as the electron donor to reduce Cr(VI) to Cr(III). [78] The effect of temperature is shown by the efficiency of reduction at 30^{o}C for 72 h was similar to that at 10^{o}C for 144 h. At low temperatures, the fluidity of the membrane decreases sufficiently to prevent the functioning of the transport systems, so substrates cannot enter the cell as rapidly, causing a low growth rate. [79] At an optimum temperature, the bacterium could utilize the substrate better, in consonance with other optimum cultural and nutritional conditions. Furthermore, temperature is known to affect the stability of microbial cell wall, its configuration, and can cause ionization of chemical moieties. [80] Isolated *Pseudomonas mendocina* used to study the chromium reduction with variation of pH, initial chromium concentrations, organic acids (alginic acid, galacturonic acid, glucuronic acid and citric acid) and their binary combinations. [81] The Cr(VI) reduction rate decreased with the increase in initial chromium concentration at optimum pH 6.0. The Cr(VI) reduction was increased in the presence of organic acids and the combination of galactronic acid and glucuronic acid showed more effective. Desorption indicated the removal of Cr(VI) due to reduction reaction instead of biosorption. [81] Similar works report using different isolated strains with variation of pH, temperature and initial concentration of Cr(VI) [82,83].

Acenetobacter calcoaciticus, a lyophilized Gram negative bacterium, was isolated from water sample taken from the Sukinda mine area of Jajpur Odisha, India. Since unfavorable pH may retard cell growth and hinder the enzymatic activity, it is an important factor in achieving the efficient Cr(VI) reduction. The reduction of Cr(VI) is highly pH dependent because protons are

significantly involved in the reduction mechanism. For a Cr(VI) reduction study *A. calcoaciticus* was grown in LB broth medium containing 100 mg/L Cr(VI) varying pH at temperature 30 ^{o}C and speed 100 rpm. The optimum pH was determined to be 8.0 where *A. calcoaciticus* reduced 85% Cr(VI) in 24 h. [84] *Pseudochrobactrum saccharolyticum* was grown in a modified LB media starting at pH 7.0 with other variable conditions. At optimum conditions of pH 8.3, initial Cr (VI) 55 mg/L, NaCl 20 mg/L, and 1.47×10^{9} cells/mL showed a complete reduction within 96 h. Electron microscopy like TEM and EDS analysis of the biomass revealed irregular and loss of shape of the cell on exposure to Cr(VI) with significant precipitation of Cr(III) both on and inside the cells. X-ray absorption spectroscopy (XAS) studies of the chromium treated bacterial cell showed a clear reduction of Cr(VI) to Cr(III). Microorganisms requiring salt for growth are referred as halophiles. Since sodium is an essential element for the ionic pumps in halophiles, the reduction rate increased with increase of NaCl up to 20 g/L [85].

Another halophile was found to be *Halomonas* species isolated from tannery effluent was able to reduce 82% of 50 mg/L Cr(VI) in 48 h. The reduction of Cr(VI) in the concomitant was visualized by discolouring of yellow colour of the medium and formation of insoluble precipitate. It showed an excellent MIC at 3500 mg/L Cr(VI) when 20% NaCl was added to the media. It favored strong Cr(VI) reduction under alkaline condition at pH 10.0. Scanning electron microscopy (SEM) analysis revealed insoluble precipitate of Cr(III) on bacterial cell surfaces further confirmed as $Cr(OH)_3$ by EDS analysis [86,87]. Similar halotolerant and toxic heavy metals tolerant tannery effluent isolate *Staphylococcus arlettae* strain could tolerate Cr(VI) up to 2000 and 5000 mg/L in liquid and solid media respectively, and reduced 98% and 75% with initial Cr(VI) concentrations of 500 and 1000 mg/L, respectively in 120 h [88].

Corynebacterium is a Gram-positive bacterium species showed resistant to high concentrations of chromate with an MIC of 22mM [89]. A multi-metal tolerant bacteria *Corynebacterium paurometabolum* isolated from chromite mine drainage was used to evaluate chromium reduction ability in 2 mM Cr(VI) in Vogel Bonner broth. The *C. paurometabolum* could reduce 62.5% of Cr(VI) in 8 days of incubation with no green precipitate of Cr(III) at pH 7.0. Presence of different cations (Zn(II), Cd(II), Cu(II), Ni(II)), anions (nitrate, phosphate, sulphate, and sulphite) and compounds (sodium fluoride, carbonyl cyanide m-chlorophenyl hydrazone, sodium azide, NN-Di cyclohexyl carboiimide) played an inhibitory effect on the reduction. Temperature showed worsening efficiency below 20^{o}C and above 40^{o}C with maximum efficiency at 35^{o}C. The carbon source was found to be a limiting factor as reduction is positively influenced by glucose and glycerol as these mimic the cellular membrane [90].

The feather-degrading *Stenotrophomonas maltophilia* produces a keratinolytic enzyme using chicken feathers as the sole carbon and nitrogen source. Addition of small amount of glucose and poly peptone to the feather medium increases the enzyme production [91,92]. A novel feather-degrading *S. maltophilia* was isolated from feather disposal site for chromium reduction study. It reduced 78% and 63% from solutions containing 50 and 100 mg/L Cr(VI) respectively in 1 h. There was no reduction of Cr(VI) when autoclaved feather protein hydrolysate was used. This shows that bacterial enzymes were not involved in the reduction process directly. The reduction was due to direct reduction of Cr(VI) by *S. maltophilia* where feather protein hydrolysate from the chicken feathers were electron donors. Cr(VI) reduction was significantly inhibited by mercury ions (Hg(II)) indicating the role of sulfur-containing amino acids in reduction process. FTIR analysis confirmed that chromium reduction occurred due to oxidation of amino acids such as cysteine and cystine [93].

Gram-negative bacteria *Acinetobacter* belongs to the wider class of *Gamma-proteobacteria* and has been employed for Cr(VI) reduction. It is a bacterium tolerant to many metals and oxygen demanding pollutants. One isolate of *Acinetobacter* sp. from aerator water of an activated sludge process at a dye and pigment industry exhibited high tolerance capacity for up to 1,100 mg/L of Cr(VI) and showed efficient chromium reduction. This *Acinetobacter* sp. was found to be very efficient and tolerant to several other metal ions in addition to Cr(VI). The MICs of this bacteria were 800, 700, 350, 600, 1100, and 1000 mg/L towards different heavy metal ions such as Ni(II), Zn(II), Cd(II), Cu(II), Pb(II), and Fe(III), respectively [94]. Another isolate of the species *Acinetobacter haemolyticus* favoured Cr(VI) reduction at the lower concentrations ranging 10 to 30 mg/L, however, incomplete Cr(VI) reduction occurred at concentrations ranging 70 to 100 mg/L. Initial specific reduction rate increased with Cr(VI) concentrations. Cr(VI) reduction was not affected by 1 to 10 mM sodium azide (a metabolic inhibitor), 10 mM of PO_4^{3-}, SO_4^{2-}, SO_3^{2-}, NO_3^- or 30 mg/L of Pb(II), Zn(II), Cd(II) ions. The TEM analysis revealed *A. haemolyticus* cells had lost its shape and size after exposure to 10 to 50 mg/L Cr(VI). The presence of electron-dense particles in the cytoplasmic region of the bacteria suggested deposition of chromium in the cells [95]. In another study the Cr(VI) reduction by an *Acinetobacter* sp. showed high tolerance up to 1100 mg/L and high Cr(VI) reducing capacity. The Cr(VI) reduction rates decreased in presence of Ni(II), Zn(II) and Cd(II). The lead ion Pb(II) did not show significant effect at lower concentration while Cu(II) and Fe(III) stimulated the rate of Cr(VI) reduction. The inhibiting effect of ions Ni(II), Zn(II), Pb(II)and Cd(II) decreased in the presence of Cu(II) and Fe(III) ions during Cr(VI) reduction in the multi-metal ions solution [96].

Gram positive bacteria *Actinomycetes* exhibit many interesting activities such as degradation and transformation of organic and metal substrates together with the production of antibiotics.

Traditionally, *Actinomycetes* have been a rich source of biotechnological products like antibiotics, industrial enzymes and other bioactive molecules [97]. Different Gram positive bacteria such as *Actinomycetes, Cellulosimicrobium* sp., and *Exiguobacterium* sp. were isolated from different chromium contaminated sites to study the efficacy of Cr(VI) reduction. One *Actinomycetes* isolate was found to reduce 82.6% and 44.3% at initial Cr(VI) concentrations of 2.5mM and 5mM , respectively, within 72 h of incubation [98]. However, *Cellulosimicrobium* sp., and *Exiguobacterium* sp. with MICs of 250 and 100 mM, respectively, reduced 45% of Cr(VI) in DeLeo and Ehrlich medium containing 10 mM Cr(VI) [99]. One aerobic bacterium *Sporosarcina saromensis* among fifty-five strains isolated from intertidal zones at low tide showed a MIC of Cr(VI) 500 mg/L in 216LB medium. The *S. saromensis* could completely reduce 100 mg/L Cr(VI) at pH 8.0 and 35 °C in 24 h. [100] Field et al. [101] used *Cellulomonas* species to assess the influence of various carbon sources, iron minerals, and electron shuttling compounds on Cr(VI) reduction. Results indicated the influence of the type of carbon source as well as electron shuttle on Cr(VI) reduction rate. The molasses as carbon source stimulated Cr(VI) reduction more effectively than pure sucrose, due to presence of more easily utilizable sugars. The Cr(VI) reduction rate increased with increasing concentration of electron shuttling compound anthraquinone-2,6-disulfonate regardless of the carbon source.

The Cr(VI) reduction potential of *Escherichia coli* was significant as it reduced 95% within 24 h when experimental parameters including pH, temperature, Fe(III) dosage, carbon source, and chelating agent, were optimized [102]. The pH-5.8 and temperature 32°C were found to be best condition when the culture medium was amended with Fe(III) and sodium citrate. The Fe(III) enhanced the reduction process by shuttling electrons from bio-reduced Fe(II) to Cr(VI) in a

coupled biotic-abiotic cycle. The addition of chelating agent sodium salt of EDTA inhibited the process.

Alkaliphilic Gram-positive bacteria *Bacillus firmus* shows potential to reduce Cr(VI) in vitro conditions [104]. The chromium reductase of *Bacillus* species was used to reduce Cr(VI) with NADH supplement as electron donor [210]. An isolated bacterium *Bacillus subtilis* could reduce Cr(VI) to Cr(III) at pH of 9.0 and initial concentration of Cr(VI) at 50 mg/L [105]. Another highly chromate-resistant *Bacillus cereus* showed MICs of 1300, 1450 and 1050 in nutrient broth, LB broth and mineral salt media, respectively. It reduced 57% within 24 h of incubation and up to 70% in further 24 h, when initial Cr(VI) concentration was 100mg/L [106]. In another study *B.cereus* reduced 73 and 92 % of Cr(VI) from tannery effluent with free cells and immobilized cells respectively, at temperature 35^{o}C and 120 rpm in 48 h [107]. An improvement in mitotic index and reduction in chromosomal aberrations was also observed in *A. cepa* grown with post-treatment effluent samples compared to untreated sample. In a bioreactor a *Bacillus* sp. was used for Cr(VI) reduction varying conditions like immobilized cells, cell free enzyme extracts, flow rate and initial Cr(VI) concentration. For immobilized cells different immobilizers such as celite, amberlite and Ca-alginate were added in to the media. With the initial Cr(VI) concentrations of 2 to 8 mg/L at the flow rates of 3 to 6 mL/hr, the immobilized cells and cell free extracts reduced 84% and 98% respectively, in the presence of celite and Ca-alginate [103].

The advantage of extracellular chromate reductase of the chromium reducing bacteria (CRB) is that it can be used under different environmental conditions, especially mining waste water. Cell free chromate reductase enzyme from a CRB *Arthrobacter* was used to determine the reduction efficiency. The enzyme was unaffected to different metals such as Mn(II), Mg(II) and Fe(III) present in a water sample of chromite mine seepage. The Cr(VI) reducing activity of the reductase

enzyme was maximized at pH range 6.5 to 7.5 and at a temperature of 35^{o}C, and was dependent on NADH [108,109]. A laboratory CRB culture *A. viscosus* was used remove Cr(VI). The experiments were conducted with both dead and live biomasses in a batch study and live biomass in a column study. From the pH variation data, pH at 1.0 favoured the Cr(VI) reduction but pH 2.0 favoured the total chromium removal in both the dead and live biomass. Contact time favoured the application of live biomass. For the column experiment, a pre-grown culture of *A. viscosus* was pumped in to the column in an up-flow method with a flow rate of 19 mL/min for 120 hrs to form a visible biofilm inside the column. Then solution containing 25 mg/L Cr(VI) at pH 2.0 was passed through same up-flow method at a flow rate of 10 mL/min continuously in ambient condition. The equilibrium of chromium uptake was achieved in 7.5 h with uptake of 20.3 mg per one gram of biofilm [110].

Desulfovibrio vulgaris Hildenborough is a model sulfur reducing bacteria (SRB) and has been shown to reduce metals, metalloids, and radionuclides [111]. The cell-mediated reduction using SRB involves hydrogenases and cytochrome c(3) as well as reduction by hydrogen sulfide. [112] *D. vulgaris* Hildenborough is capable of reducing Cr(VI), but cells are unable to use Cr(VI) as a terminal electron acceptor linked to growth. [113] *D. vulgaris* strain was used to study the Cr(VI) reduction ability in the presence of the Fe-bearing minerals hematite, aluminum substituted goethite (Al-goethite), and nontronite (NAu-2). Also an abiotic Cr(VI) reduction was conducted in dithionite reduced NAu-2 or iron sulfide (FeS). The pseudo first order reduction of Cr(VI) was observed in microcosms containing *D. vulgaris* strain and hematite/Al-goethite, and the rate constant was found to be 1.49 hr^{-1}. The microcosms containing only *D. vulgaris* strain without hematite pseudo first order rate constant was 0.56 hr^{-1}. But the combination of NAu-2 and microcosms containing *D. vulgaris* strain showed decreased reduction due to toxicity of high

concentration of Al(III) present in the mineral aid. There was significant initial loss of Cr(VI) in mineral aid due to adsorption, and significant Cr(VI) instead of Cr(III) was found in the resulting solids. [114] In another study *D. vulgaris* showed lag period of approximately 30 h in presence of 0.05 mM Cr(VI), though Cr(VI) was reduced within the first 5 h without growth of the strain [115]. During the lag period small amounts of lactate were still utilized without sulfate reduction or acetate formation. After 40 h of incubation sulfate reduction occurred concurrently with the accumulation of acetate and production of hydrogen due to bacterial activity. The lag period was prevented by addition of ascorbate to Cr(VI) exposed *D. vulgaris* culture medium. Addition of pyruvate displayed more tolerance to Cr(VI) exposed *D. vulgaris* culture medium compared to lactate.

Co-existence of the different toxic metals is common in high temperature environments (up to 70 ^{o}C). Results Thermophiles have potential application in metal bioremediation at high temperature subsurface radioactive waste disposal sites, effluents from refractory and metallurgical industries and other high temperature wastes. Despite significant progress on iron reduction by thermophilic microorganisms, studies on the ability of these bacteria to reduce toxic metals are still limited. *Deinococcus geothermalis*, a radiation-resistant thermophilic bacterium and *Bacillus thermoamylovorans*, a moderately thermophilic and facultative anaerobic bacterium have showed Cr(VI) reduction ability [116,117]. Thermophilic methanogen obligate *Methanothermobacter thermautotrophicus* was used to reduce Cr(VI) with H_2/CO_2 as substrate containing various Cr(VI) concentrations ranging from 0.2 to 5 mM. The thermophile *M. thermautotrophicus* showed complete reduction up to 0.4 mM Cr(VI). SEM and TEM analysis of *M. thermautotrophicus* cells after Cr(VI) exposure found both extra- and intracellular chromium reduction mechanisms [118].

5.2 Fungi

Fungi have unique properties which sustain them in toxic metal contaminated sites due the presence of cell wall material within that shows excellent metal-binding properties. The enzyme-mediated activity of fungi provides sufficient metabolites to treat wastewaters. The enzymes are produced during all phases of the fungal life cycle unlike bacteria and irrespective of pollutant concentrations [119]. In addition to extracellular enzyme production, fungal biomass has been identified as a most effective adsorbent for accumulation of toxic metals, such as Cr, Cu, Hg, Ni, Cd and Pb, from wastewaters [120,121]. Fungi species are known to detoxify toxic metals by several mechanisms including extra and intra cellular precipitation, redox reaction and active uptake [122-124] Different metabolic products of fungi like phosphate, proteins, and nitrogen-containing ligands on protein, chitin and chitosan also influence the toxic metal uptake [125,126]. The fungi can adapt and grow under high metal concentrations and in various extreme conditions of temperature, nutrient availability and pH. [127] A chromium resistant fungal strain *Fusarium* isolated from the contaminated soil of a tannery effluent was used for a Cr(VI) reduction study. [70] The isolated fungal strain reduced all Cr(VI) at an optimum condition of temperature 25^{o}C, incubation time 72 h and pH 5.0. Protein expression profile showed exposure of the fungal cell to chromium. Different micro imaging analyses revealed enhanced surface roughness, significant swelling and formation of cage like structures on the cell surface induced by Cr(VI).

Another study, five out of the twenty fungal strains (*Penicillium commune, Paecilomyces lilacinus, Cladosporium perangustum, Cladosporium perangustum* and *Fusarium equiseti*) isolated from soil, sludge and wastewater samples of a tannery industry area showed high Cr(VI) tolerance with MIC above 500 mg/L. Consortium of the five fungal strains were inoculated in a 1 L bioreactor with supplement of 1% glucose and 0.01% ammonium nitrate to remove chromium from the

tannery wastewater sample containing Cr(VI) 9.86 mg/L and total chromium 12.26 mg/L. The fungal consortium removed 73 % of Cr(VI) from the wastewater sample in 12 h [75]. Various fungal strains of *Aspergillus* such as *A.niger, A.flavus*, *A.fumigatus*, *A.nidulans*, *A.heteromorphus*, *A.foetidus*, and *A.viridinutans* isolated from different contaminated soil samples of a tannery industry wastewater were used individually for Cr(VI) removal from wastewater from the same industry. With the conditions of pH 3.0, fungi biomass 4 g and initial Cr(VI) concentration 18.1 mg/L the order of Cr(VI) removal efficiency of the individual strain was as: *A. niger* >*A. flavus* >*A. umigates* >*A. nidulans* >*A. heteromorphus* >*A. foetidus* >*A. viridinutans. A. niger* removed a maximum of 96.3 % of Cr(VI). The MIC of the fungal strains followed a same order of Cr(VI) removal efficiency [128]. Singh et al. [129] used *A. flavus* for Cr(VI) reduction from simulated wastewater with Fe(II) ion supplement. The Fe(II) addition significantly enhanced both chromium removal as well as stickiness of the biomaterial. A fungal consortium of *A.lentulus, A.terreus* and *Rhizopus oryzae* were used for removal of two heavy metal ions (Cr(VI) and Cu(II)), and two dyes (acid blue 161 and pigment orange 34) from a mixed waste stream. *A. terreus* alone proved better at Cr(VI) removal. The mixed consortium removed 100 % Cr(VI) which was higher than that achieved individually. The complexity of metal-dye mixtures observed in the individual fungus run, but performance of the mixed consortium was unaltered [130].

5.3 Phyto species

Biotechnology is drifting towards phytoremediation for cleaning up contaminants. Plants have ability to uptake soluble metal ions from water and soil moisture during photosynthesis [131,132]. In addition to the up-taking of metal ions, plants have ability to detoxify metals to less harmful

forms, either by chelating heavy metals or changing oxidation states [133]. The phytoremediation process is more challenging than its first appear because choosing a plant species for a particular environment is the most important factor and can be difficult. Plants are very sensitive toward toxic metals due to their selectivity towards different metals. Plants depend on properties of ecosystem in terms of the rate of biomass production [134]. Three plant species such as *Phragmites australis, Salix viminalis* and *Ailanthus altissima* were irrigated by contaminated water containing 10 mg/L Cr(VI) in a continuous process for 360 days to evaluate the chromium reduction efficiency. *P.australis* and *S.viminalis* removed 56 % and 70 % of total chromium from water, respectively. However, the efficiency of *A.altissima* was not significant. The contaminated dry soil analysis revealed the removal efficiency from the soil with initial chromium concentration of 70 mg/kg to 32, 36, and 41 mg/kg for *S.viminalis*, *P.australis*, and *A.altissima*, respectively. The mechanism of chromium removal was confirmed on the basis of reduction of Cr(VI) as adequate Cr(III) found in all plant tissues. Highest chromium translocation potential of *P.australis* and *S.viminalis* was found respectively from roots to stems and roots to leaves. Of the three plant species Salix can withstand with higher chromium concentration [135,136]. In another study *Halimione portulacoides* was planted to uptake and reduce Cr(VI). The anti-oxidative feedback and biomarkers were studied using hydroponics mesocosmos approach. *H.portulacoides* could reduce 40% Cr(VI) from the medium containing 15 mg/L initial concentration, however, the reduction efficiency increased to 60% when initial Cr(VI) concentration was 30 mg/L. The Cr(VI) was accumulated in the roots and aboveground organs of the plant. Chromium in the chlorophyll and flavonoid proved consequences in the photosynthetic and photo-protective mechanisms [137].The biomass of aquatic plant *Hydrilla verticillata* is known as a hyper accumulator of toxic metals like Hg, Cd, Cr and Pb [138]. Biosorption potential of Fenton modified dried biomass

(FMB) of *H.verticillata* was investigated to remove Cr(VI) and Ni(II) ions from wastewater using an up-flow packed-bed column reactor. Within the optimized design parameters of the column reactor such as bed height of 25 cm, flow rate 10 mL/min, initial metal ion concentration 5 mg/L and particle size range of FMB 0.25 to 0.50 mm, the biosorption efficiencies for Cr(VI) and Ni(II) uptake were 89 and 87 mg/g, respectively. Column regeneration experiments using 0.1 M HNO_3 showed good reusability of FMB for ten cycles of sorption and desorption. [139] Dried twigs of *Melaleuca diosmifolia* fallen from the plants were used to detoxify and remove Cr(VI) from aqueous solution. The gas chromatography of dried twigs revealed the presence of natural sources of eucalyptol which contained high concentrations of reducing compounds like iron, phenols and flavonoids. Batch studies revealed 5 g/L of dried twigs able to remove 97 to 99.9 % Cr(VI) from the solution containing 250 mg/L when the pH ranged from 2 to 10 and temperature from 24^{o}C to 48^{o}C. From the well fitted Langmuir adsorption isotherm the monolayer adsorption capacity was 62.5 mg/g. The inductively coupled plasma optical emission spectrometry and liquid chromatography analyses of the aqueous and solid phases revealed an adsorption-coupled reduction mechanism of Cr(VI). Further SEM, IR and XRD analyses of the biosorbent before and after adsorption process also confirmed reduction of Cr(VI) to Cr(III) followed by complexation onto functional groups of the active surface. The removal efficiency of Cr(VI) was 99% from lake and sea water samples. [140]

5.4 Algae

Photochemical reduction of Cr(VI) is a regular practice for remediation of toxic chromium components from the environment. Biomass of algae species *Chlorella vulgaris* has shown

efficiency toward Cr(VI) reduction. This has encouraged interest in employing algal community to reduce the toxic Cr(VI) from contaminated water and soil. Several efforts have been made to reduce Cr(VI) into less toxic Cr (III) by algae as it is available conveniently and less expensively. [141,142] A laboratory salt tolerant microalgae *C.vulgaris* grown in algal culture medium was used to remove different pollutants in tannery wastewater with 1:1 dilution with tap water. The tannery wastewater contained 3.22 mg/L Cr(VI) along with other pollutants. At 28 °C under fluorescent lights of 150-300 μmol photons/m^2/s, the microalgae completely removed Cr(VI) from the diluted water sample in 12 days. [143] However, the functional role of organelle inside the algal cell for Cr (VI) reduction was poorly understood. Chen et al. [144] extracted organelles in green algae *C.vulgaris* and further treated for Cr(VI) reduction tests. They observed chloroplasts not only adsorbed 21% of total chromium but also reduced 70% of Cr(VI) in comparison to the abiotic control run. Further the isolated thylakoid membrane showed better Cr(VI) reduction potential with the presence of sodium alginate, even though the Hill reaction activity was inhibited. As per photosystem II, the addition of mesoporous silica (SBA-15) enhanced the reduction ability through improving the light-harvesting complex II efficiency and electron transport rate. The organelles of *C. vulgaris* not only offered a basement to mechanism of the Cr (VI) reduction, but also provide a new sight for removal of heavy metals from contaminated water. [144]

Macro-alga *Sargassum cymosum* has been used as an electron donor for the reduction of Cr(VI). It was used sequentially through the oxidation of the biomass initially followed by as a natural cation exchanger for the chromium sequestration. [145] *S. cymosum* reduced 3.0 mM of Cr(VI) while dosed with 1 g of biomass. The FTIR analysis and potentiometric titration techniques revealed association of weak acidic carboxylic groups on the surface of the biomass as the main mechanism of the sequestration of Cr(III). The binding sites on the surface of biomass were formed

due to the oxidation of biomass during Cr(VI) reduction. In another study, brown macro alga *Pelvetia canaliculata* was used as a natural electron donor for the reduction of Cr(VI) from acidic electroplating wastewater. The Cr(VI) reduction capacities of raw and protonated *P. canaliculata* were found to be 1.8 and 2.3 mmol/g, respectively. The Cr(III) uptake capacities of the oxidized biomass were 0.8 and 1.9 mmol/g, respectively. In the continuous column reactor packed with raw *P. canaliculata,* 2.1 mmol/g Cr(VI) was reduced. [146]

5.5 Plant nuts

Scale-up studies of bioremediation are usually done using thick packed bed column reactors. Direct use of microbial biomass to develop a free cell packed bed column reactor is not easy due to the low mechanical strength and small particle size of the free cells. Excessive hydrostatic pressures are required to maintain a suitable flow rate in order to withstand the packed bed inside the column. [209] Further, the immobilized cell biomass in a carrier material was found to be more efficient than free cell biomass in the bioremediation. [147] In this context, olive stones discarded from an olive cake industry were collected and milled into a powder form of size less than 1.0 mm. The olive stone powder was used as adsorbent for biosorption of Cr(VI) from a 10 mg/L synthetic solution in a batch reactor at pH 2.0 and temperature 25^{o}C for 5 h. According to chromium chemistry, Cr(VI) is stable as H_2CrO_4 at low pH as the H^+ ion protonate the surface of adsorbent resulting in the adsorbent becoming positively charged. This positive adsorbent has strong affinity to the negatively charged $HCrO_4^-$ resulting increased Cr(VI) removal at lower pH. When the pH increased, the surface of adsorbent is negatively charged due to decrease of proton concentration resulting less affinity for the adsorption of $HCrO_4^-$. High-resolution XPS spectra revealed Cr(III)

bound to the olive stone powder concluding the removal of Cr(VI) from acidic solution is a coupled biosorption-reduction reaction. This was further confirmed by the desorption test with deferent reagents H_2SO_4, NaOH, HNO_3, HCl, CH_3COOH and HOOCCOOH. [148]

Lakshmanraj et al. [149] used boiled mucilaginous seeds of *Ocimum americanum* to investigate chromium removal efficiency from Cr(VI) solutions. The initial concentration of Cr(VI) in the solutions were 10 mg/L, 20 mg/L and 40 mg/L for different run with the biosorbent dosage of 8 g/L dry seeds at a pH 1.5. The authors also proposed the removal mechanism as biosorption-reduction coupled process. The biosorption data fitted well with Langmuir adsorption isotherm. The Cr(III) uptake was found to be 32 mg/g of dry seeds. The continuous column reactor packed with boiled mucilaginous seeds as adsorbent bed reduced 80 % of Cr(VI) at a flow rate of 27 mL/hr with the initial concentration of 25 mg/L Cr(VI) in the feed solution. However, uptake of Cr(III) from the aqueous solution was 56.25%. In another study mosambi (*Citrus limetta*) peel dust was used for removal of Cr(VI) from aqueous solutions. [150] Batch adsorption study showed similar reduction coupled adsorption as described by Lakshmanraj et al.[149]. The optimum condition were found to be an adsorbent concentration of 20 g/L, pH of 2.0, equilibrium time of 2 hrs, and temperature 40 ^oC for Cr(VI) removal.

5.6 Biochar

The thermal decomposition of organic biomass at low temperature and limited oxygen supply generates a byproduct which is rich of activated carbon known as biochar. In recent years, biochar has attracted research interest because of its unique capacity of remediating contaminants from soil and water. [151, 219] Biochar usually contains carbon between 30% and 70%. The carbon is

a source of protons essential for the reduction of Cr(VI) and acts as an immobilizer for the Cr(III). [152] The applications of biochar include: (i) potential carbon sequestration agent in soil, (ii) adsorbent of heavy metals in soil and aqueous solutions, (iii) micro and macro nutrients sink in soil, thereby reducing their leaching losses, and (iv) soil fertility and productivity enhancer. [153-156] Biochar stimulates soil microbial communities which enhance the production of protons for Cr(VI) reduction reactions. The biosorption coupled with a reduction reaction by biochar is enhanced due to the physical and chemical properties such as having a high surface area with oxygenated functional groups. [157-159]

Ramie residues of decorticated stems of ramie plant were air dried room temperature. Then they were smashed to pass through a 149 micron sieve followed by pyrolysis at 300, 450, and 600 ^{o}C in a muffle furnace under nitrogen atmosphere inside. The biochars were washed with deionized water and then dried at 60 ^{o}C for 24 h followed by sieving to a size 60.15 mm. Biochar of 100 mg was added in a sealed conical flasks containing 50 mL of Cr(VI) solution on a thermostat water-wash shaker at 160 rpm. The adsorption efficiency decreased with increasing pyrolysis temperature due to a higher aromatic structure and fewer polar functional groups were observed for biochar at high pyrolysis temperature. Low temperature biochar favored chemical adsorption due to presence of carboxyl and hydroxyl groups. The adsorption coupled reduction mechanisms concluded that Cr(VI) ions were electrostatically attracted by the positively charged biochar surface and then reduced to Cr(III). [160]

A study involved native *Macadamia* activated carbon which was cross-linked on the surface with epichlorohydrin, grafting diethylenetriamine and triethylamine to prepare the amino-modified activated carbon for adsorption of Cr(VI). With the optimum condition of pH 5.0, contact time 2 h, initial Cr(VI) concentration 100mg/L and adsorbent mass 0.10 g, more than 90% Cr(VI) was

adsorbed on the surface of amino-modified activated carbon adsorbent. [161] Bioremediation of Cr(VI) was conducted with three manures from poultry (PM), cow (CM) and sheep (SM), three respective manure-derived biochars (PM biochar (PM-BC), CM biochar (CM-BC) and SM biochar (SM-BC)) and two surface modified biochars (modified PM-BC (PM-BC-M) and modified SM-BC (SM-BC-M)). Chitosan and zerovalent iron (ZVI) were used for surface modification of the biochars during the pyrolysis. The surface modified biochars exhibited enhanced properties for Cr(VI) reduction. The authors have illustrated an impressive design (figure 4) suggesting the Cr(VI) reduction by the surface modified biochars. [162]

6. Biostimulation

Modification of the environment to stimulate the growth of existing bacteria during bioremediation is called biostimulation. This requires addition of various nutrients and electron acceptors or donors. The microbial reduction of Cr(VI) can be enhanced by the addition of electron donors like acetate, lactate, or molasses as the mechanism have been discussed earlier. [163,164] The efficiency of different electron donors in biostimulation depends on the indigenous microbial communities and the physicochemical characteristics of each site. This plays an important role in kinetics of the microbial growth and heavy metal reduction in specific environments. Anaerobic biostimulation was used to assay the Cr(VI) reduction for soil digested chromium solution in three different ways such as (i) soil with acetate to test biological reduction (biostimulated soil); (ii) sterilized soil with acetate to determine abiotic reduction triggered by acetate (control); and (iii) soil with only water as a second control, at alkaline pH range. [165] In the first case 16 mM Cr(VI) was reduced to zero in 25 days with only 18% acetate consumption, however no significant result

were found in other two cases. Among four species isolated from the soil only *Halomonas* sp. showed Cr(VI) resistant by 16S rDNA gene amplification and sequencing with MIC of 32 mM.

In a sequencing batch reactors, Cr(VI) reduction study from a ground water was done to evaluate the efficacy of an aerobic and anaerobic system using mesophilic anaerobic digested sludge and aerobic activated sludge from a wastewater treatment plant as inoculums. Cr(VI) played as an electron acceptor and reduced to Cr(III) in the anaerobic system resulting more that 98% of Cr(VI). In case of aerobic system oxygen was the competitive electron acceptor to Cr(VI) resulting reduction of O_2 to oxide ion resulted lacking of Cr(VI) reduction. [166] Anaerobic and anoxic conditions were employed to determine the Cr(VI) reduction ability in two sequencing bioreactors (SBR) fed with groundwater of 3L (total volume of reactor=5 L). The design parameters were 0.5 h feeding time, 22 h reaction time, 1 h settling time and 0.5 h decanting time, and a sludge retention time (SRT) of 10 days. The nominal hydraulic residence time of the SBRs was equal to 1.7 days. The substrate (90% sugar and 10% milk on a COD basis) concentration of 200mg/L, and sufficient N and P were added to each SBR. Potassium nitrate as bind oxygen was added to anoxic reactor. Both the reactors were inoculated with a mixture of mesophilic anaerobic digested sludge and aerobic activated sludge from a WTP at a ratio of 1:1 on a mass basis. More than 99% Cr(VI) was reduced to Cr(III) in both the anaerobic and anoxic conditions with initial Cr(VI) concentrations of 1.8 and 10 mg/L, respectively. Anoxic conditions showed better reduction efficiency with increasing initial Cr(VI) concentration. The variation of initial Cr(VI) concentration on the mixed liquor volatile suspended solid production showed no change up to 1.5 mg/L of Cr(VI), but, microbial growth was inhibited up to 65 % in both the conditions for initial Cr(VI) concentrations 20 mg/L. [167]

Since bioimmobilization plays a significant role on microbial growth, a series of microcosm experiments were conducted using a range of commercial electron donors on the basis of degrees of lactate polymerization (polylactate) for reduction of Cr(VI) from waste water. [163] The experiments were conducted using sediments immersed in groundwater with Cr(VI) amendment. Several types of lactate-based electron donors (hydrogen release compound, HRC; primer-HRC, pHRC; extended release HRC) and the polylactate-cysteine (metal remediation compound, MRC) were used as electron donors. The polylactate compounds stimulated the bacterial biomass and activity better than that of sodium lactate with equivalent carbon concentrations in both the acetates. With the microbial growth concentrations of headspace hydrogen and methane increased. Enrichment of *Pseudomonas* sp. occurred with all types of lactate additions, and enrichment of sulfate-reducing *Desulfosporosinus* sp. occurred with almost complete sulfate reduction. The electron donors such as pHRC and MRC showed effective Cr(VI) removal from the solution.

The effect of the carbon source on microbial community structure in the batch cultures derived from industrial sludge and Cr(VI) reduction was studied in aerobic batch reactors containing industrial sludge amended with two different carbon sources such as sodium acetate and sucrose separately. From sodium acetate to sucrose led to a 5 to 9.5-fold increase in biomass and to a 1.3 to 2.1 folds increase in chromium reduction rate. Bacterial species such as *Acinetobacter lwoffii, Defluvibacter lusatiensis, Pseudoxanthomonas japonensis, Mesorhizium chacoense,* and *Flavobacterium suncheonense* were developed when sodium acetate was amended. Fungal strains such as *Trichoderma viride* and *Pichia jadinii* when sucrose was amended. [168] Isotopic $^{13}CH_4$ as the sole electron donor with an aerobic methane oxidizing (AOM) archaea in batch experiments and long-term performance in the reactor showed that Cr(VI) reduction was coupled with methane oxidation. High-throughput sequencing of the 16S rRNA genes demonstrated that the microbial

community had changed substantially after Cr(VI) reduction. The populations of ANME-2d archaea were enhanced during operation. They became the only predominant AOM-related microbe showing the Cr(VI) reduction was on the basis of anaerobic oxidation of methane. [169] FerroOrozco et al.[170] reported synergistic Cr(VI) reduction by addition of powdered activated carbon (PAC) to a bioreduction process using aerobic activated sludge (AS). The result showed synergistic Cr(VI) removal using the AS-PAC system compared to either AS or PAC individually. However, the presence of only PAC did not enhance the growth of biological community.

7. Microbial Fuel Cell

Microbial fuel cells (MFC) are an emerging technology combining microbiologically-catalyzed reduction reaction with a biocathode. AMFC was recently shown to reduce Cr(VI) in an autotrophic environment and simultaneously harvest electricity during the treatment process. [171,172] Biocathode MFCs using electrochemically active microorganisms as catalytic centers at both the anode and cathode show great promise in Cr(VI) bioremediation. Their operation is inexpensive, the catalysts can self-regenerate and the power supply is sustainable. Biocathodes using microorganisms as catalysts to transfer electrons from the cathode to electron acceptor, similar as the bioanode require an enriched electron-accepting (electrotrophic) biofilm on the surface, formed via acclimatization. In a dual chamber MFC with wastewater inoculums, Cr(VI) reduction was performed by setting the biocathode potential at -300 mV and the results were compared with the data for MFC with no applied potential. With the set potential run, the startup time reduced to 19 days with Cr(VI) reduction rate 19.7 mg/L/d and the maximum power density 6.4 W/m^3. In the MFC without set potential, the results were much deteriorated as 26 days startup

time, reduction rate 14.0 mg/L/d and power density 4.1 W/m^3. The result of MFC with -150 mV set potential was similar to that of -300 mV. But the set potentials of +200 mV and -450 mV showed an alteration in the output current density [173]. In another dual chamber MFC the reaction time required for the complete removal Cr(VI) of 300 mg/L, 150 mg/L and 75 mg/L were 1,350 min, 750 min and 180 min, respectively, at a pH of 2.0. [174] In an MFC system, acetate oxidizing mixed anaerobic culture brought from an anaerobic digester was enriched in anode compartment and a mixture of denitrifying and anaerobic mixed cultures was enriched in the presence of Cr(VI) as catholyte in cathode compartment. The anode and cathode chamber was separated by a proton exchange membrane. Four consecutive Cr(VI) spikes were carried out to investigate the effect of initial Cr(VI) concentration on the reductive activity of the microorganisms and power generation. The catholyte was replenished with fresh medium before the addition of Cr(VI) at each spike. The pH of catholyte and anolyte were maintained ranging from 7.2-7.6 and 6.9-7.2, respectively. The Cr(VI) reduction followed zero order kinetics due to limitations in protons migration through the proton exchange membrane and electrons through the external resistance. The power generation had a direct relationship with initial Cr(VI) concentration and the specific reduction rate as the reduction rate decreased with the increasing the initial concentration of Cr(VI) due to inhibitory growth of microbe at high Cr(VI) concentration or accumulated Cr(III) or combined effect of both. This was further confirmed by the analysis of the residue and filtrate of the catholyte [175]. A similar type of work has been reported in which synthetic 100 mg/L Cr(VI) containing wastewater as catholyte and anaerobic microorganisms as anodic biocatalyst [176]. The maximum power density of 150 mW/m^2 and the maximum open circuit voltage of 0.91 V were generated with Cr(VI) as the electron acceptor.

A dual-chamber MFC was constructed from two plexiglass cubic chambers (liquid volume of each chamber was 70 mL) and both chambers were kept air tight. The chambers were separated by a proton exchange membrane. A graphite sheet was used as electrode in a unique way as first for the anode chamber followed by cathode after complete acclimatization in the anode chamber and this process is referred as 'ex-situ MFC'. Different anolyte and catholyte were used with anaerobic activated sludge as inoculums. The in-situ MFC process was a regular dual chamber MFC having two graphite sheets inserted in the anode and cathode simultaneously. The ex-situ MFC which used ex-situ acclimatization on biocathode initially produced a voltage of 290 mV which dropped to 17.9 mV after 24 hrs. In comparison, the in-situ MFC which used in-situ acclimatization on biocathode achieved a maximum voltage of 178 mV, which decreased by 38.5% less than that of the ex-situ analog. Anode potentials remained similar and stable between 455 and 449 mV during the operations in both ex-situ and in-situ MFCs, implying the robust activities of anode biofilms. Thus, the variations in voltages were mainly attributed to the performances of cathodes. The maximum power density of the ex-situ MFC was 9.7 mW/m^2 at a current density of 69.7 mA/m^2, 1.2-fold that of the in-situ MFC. The ex-situ MFC showed a higher Cr(VI) reduction rate of 0.66 mg/L/hr which was 2.9 times higher than that obtained from the in-situ MFC. After 24 hrs of operation the removal of Cr(VI) was 79.3 % for the ex-situ MFC, which was 20 % higher than that in the in-situ MFC. The Cr(VI) reducing strain *Gamma-proteobacteria*was found in the ex-situ biocathode. The number of strains in the ex-situ biocathode was much higher than that in the in-situ biocathode. This demonstrated that in the MFCs these bacteria were exoelectrogenic on bioanodes to oxidize organics and electrotrophic on biocathodes to reduce Cr(VI). [177]

For simultaneous electrochemical reduction of Cr(VI) in water and generation of bioelectricity, Alumina/nickel nanoparticles dispersed carbon nanofiber (CNF) based electrodes were used in a

mediator less dual-chamber MFC. The alumina nanoparticles increased the electrical conductivity of the electrode. The Ni nanoparticles served as the catalyst for growing the CNFs on an activated carbon microfiber substrate by chemical vapor deposition and for catalyzing the Cr(VI) reduction at the cathode. The MFC showed a complete removal of Cr(VI) at 100 mg/L concentration with reduction rate of 2.13 g/m^3/hr and generated power density of 1540 mW/m^2 with an open circuit potential of 900 mV and cathodic columbic efficiency of 93 %. [182] In a similar work, a graphene/biofilm was constructed by amending glucose with grapheme oxide solution first for anode action followed by cathode action in same pot. The maximum power density of the MFC with a graphene biocathode found to be 5.7 times greater than that of the dual-chamber MFC with a graphite felt biocathode. The Cr(VI) reduction was enhanced in the one-pot MFC resulted 100% removal of Cr(VI) of 40 mg/L concentration in 48 hrs compared to 58.3 % only in the dual-chamber MFC. [178]

Plant-microbial fuel cell was used to reduce Cr(VI) and the performance was investigated by varying initial concentration of Cr(VI). In a typical design of plant-microbial fuel cell, Ryegrass (*Lolium perenne*) was chosen because of its rapid growth and large biomass, and its fibrous root system with a dense rhizosphere. Greenhouse grown, healthy and identically sized Ryegrass plants were transplanted into parallel plant-microbial fuel cell reactors under various operation conditions for comparison. The reactors were fed with ½ Hoagland's solution and sodium acetate as the electron donor. More than 90% of Cr(VI) was reduced in the plant-microbial fuel cell at various initial Cr(VI) concentration. Interestingly, the reduction efficiency increased with increase of initial Cr(VI) concentration unlike other MFC as discussed above. There was a linear relationship between the current density with the reduction rate observed as a higher initial Cr(VI) concentration. The comparison of the results between the biotic plant-microbial fuel cell and

abiotic control experiment showed the contribution of bioelectrochemical reduction to Cr(VI) removal was phenomenal. [179] Figure 5 shows the schematic diagram of plant-microbial fuel cell proposed by the authors.

Reduction of Cr(VI) from contaminated water was investigated using a modified MFC with KCl agar salt bridge and anaerobic microorganisms as the anodic biocatalyst. The cathode was an abiotic system. This salt bridged MFC could reduced 100% and 80% of Cr(VI) when initial Cr(VI) concentration were 5 and 10 mg/L, respectively in 19 days. The MFC system with 5 mg/L of Cr(VI) generated a maximum of power density 92.65 mW/m^2 and voltage of 0.35 V. With 10 ml/L Cr(VI), the results were 75.08 mW/m^2 and 0.103 V. The advantages of the salt bridge are less complexity and a lower cost in place of expensive membranes like nafion and an abiotic cathode. [180,181]

8. Conclusion

The review focus on the source of chromium in the environment, its toxicity to the biotic components, chemistry behind the enrichment of Cr(VI) in the water systems, resistivity mechanism of microorganisms, and recent trend of the bioremediation of Cr(VI) from water environments. Different anthropogenic activities such as chromite or ferrous-chromite mining, leather tanning, pigment synthesis, electroplating and metal finishing are causes of the enrichment of Cr(VI) in the water systems. Cr(VI) causes toxicity in the living organisms in terms of cellular reduction of Cr(VI) to Cr(III). The reactive species generation inside cells, Cr(III)-protein coordination complex formation, DNA damage, can contribute to carcinogenicity. Further absorption on the stomach wall, effects on sperm productivity, carcinomas of the bronchial

systems, and neurotoxicity can be seen in humans. Cr(VI) removal from water is possible by reducing the chemical species to less soluble Cr(III) followed by hydration to solidify the reduced species rather than direct precipitation of Cr(VI). Adsorption of Cr(VI) is possible by attachment on the functional mass of some live or dead cells. Bacteria, fungi, plant species and nuts, algae have shown capability to bioreduce or biosorp or reduce via coupled adsorption due to their versatile life cycles. A wide range of bacteria- direct chromium reducing bacteria, sulphur and iron reducing bacteria and engineered bacterial profile - have shown effective bioreduction in a variety of conditions including pH, temperature, contact time, agitation, nutrient medium, redox stimulating reagents, carbon and nitrogen sources, immobilizers, free cell reductase and many more. Fungal consortium, plant species and algae have also proved the Cr(VI) can be reduced by a reduction coupled adsorption mechanism. They too can operate under varying different conditions of adsorbents and adsorbates speciation, pH, temperature, nutrient availability, functional induction of adsorbents and surface modifications. Laboratory scale microbial fuel cells are employed to reduce Cr(VI) from water gains a new light of the reduction-cum-electricity generation technique. Inadequate reports regarding the scale-up test of the Cr(VI) bioremoval suggests that more focus should be given in the pilot and industrial scale.

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Table 1. Standard parameters of toxic metal in drinking water. [3,4]

Contaminant	USEPA standard		Indian Standard	Potential Health Effects from Long-Term Exposure Above the MCL	Sources of Contaminant in Drinking Water
	Maximum Contaminant Level Goal (MCLG) in mg/L	Maximum Contaminant Level (MCL) in mg/L	Maximum Contaminant Level (MCL) in mg/L		
Antimony	0.006	0.006	-	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
Arsenic	0	0.01	0.05	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes
Barium	2	2	-	Increase in blood pressure	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits
Beryllium	0.004	0.004	-	Intestinal lesions	Discharge from metal refineries and coal-burning factories; discharge from electrical, aerospace, and defense industries
Cadmium	0.005	0.005	0.003	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints

Total Chromium	0.1	0.1	0.05 as Cr(VI)	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Copper	1.3	1.3	-	Short term exposure: Gastrointestinal distress Long term exposure: Liver or kidney damage People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	Corrosion of household plumbing systems; erosion of natural deposits
Lead	zero	0.015	0.01	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits
Mercury	0.002	0.002	0.001	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Selenium	0.05	0.05	-	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines
Thallium	0.0005	0.002	-	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from ore-processing sites; discharge from electronics, glass, and drug factories

Table 2. Chromite mineral commodity summaries of 2016 by United States Geological Survey [12]

Country	Mine production for the year 2014 and 2015 ($\times 10^3$ metric ton)		Shipping grade reserves ($\times 10^3$ metric ton)
	2014	2015	
Kazakhstan	3700	3800	230000
South Africa	12000	15000	200000
India	3540	3500	54000
Turkey	2600	3600	Not applicable
Other countries	4,590	4,600	Not applicable
United States	Not applicable	Not applicable	620
World total (rounded)	26,400	27,000	>480,000

Table 3. List of foods contain chromium. [9]

Food	Cr content (μg per 100 g food)
Brewer's yeast	112
Liver	55
Whole-wheat bread	42
Wheat bran	38
Rye bread	30
Potato	24
Wheat germ	23
Egg	20
Green pepper	19
Apple	14
Butter	13
Cheese	13
Banana	10
Carrot	9
Navy bean, dry	8
Fresh fish	6
Orange	5
Blueberry	5
Green bean	4
Cabbage	4

Table 4. Chromium content in human body. [7]

Organ/Tissue/Fluid	Total Chromium concentration
Serum	0.01-0.38 µg/L
Blood	0.12-0.67 µg/L
Urine	0.05-1.80 µg/L
Saliva	0.55-0.70 µg/L
Breast milk	0.06-1.56 µg/L
Lung	130-1375 µg/kg
Liver	5-15 µg/kg
Spleen	7-29 µg/kg
Nail	0.52-172.92 mg/kg
Hair	0.234-3.80 mg/kg
Teeth	7.20-35.00 mg/kg
Skeleton	5-15 µg/kg
Muscle	5-10 µg/kg
Skin	50-200 µg/kg
Average amount per human body	0.4-6 mg

Table 5. List of isolates from different sources and their applications in Cr(VI) process.

Cr(VI) reducing Biota	Source of Cr(VI) with concentration	Reduction process and efficiency	Reference
Acenetobacter calcoaciticus isolated from chromite mine	Synthetic $K_2Cr_2O_7$ solution, 100 mg/L	100 mL Luria Bertani medium in 250 mL Erlenmeyer flask; conditions: temp.-30 ^oC, 100 rpm, incubation time-24 hr and pH-8; Efficiency-85%	[84]
Fusarium genus isolated from tannery effluent	Synthetic $K_2Cr_2O_7$ solution, 10 mg/L	Potato dextrose broth media in 250 ml Erlenmeyer flask; optimum condition: temp.-25 ^oC, incubation time-72 hr, 120 rpm and pH-5; Efficiency-100%	[70]
Halomonas species isolated from Cr contaminated soil	Soil digested Cr(VI) solution, 18 mM	15 g soil digested in 30 mL sterile water in 300 mL bottle contains; (i) acetate dependent biostimulated soil, (ii) acetate dependent abiotic reduction, and (iii) soil in water without acetate; Efficiency-100%	[165]
Plant (*Phragmites australis* and *Ailanthus altissima*)	Tap water, 10 mg/L	Pots in Greenhouse; conditions: temp.-20 °C, average relative humidity-60 %, irrigated time-360 days, continuous flow rate-0.2 L/min using peristaltic pump; Efficiency: 50% for *Phragmites australis* and 40 % *Ailanthus altissima*	[136]
Amino modified activated carbon from native *Macadamia*	Synthetic $K_2Cr_2O_7$ solution, 10 to180 mg/L	100 mL beaker; conditions: pH, contact time, initial Cr(VI) concentration and adsorbent dosage; Efficiency-100%	[161]
Cellulosimicrobium sp. and *Exiguobacterium* sp. isolated from contaminated soil	Synthetic $K_2Cr_2O_7$ solution, 10 mM	DeLeo and Ehrlich medium; conditions: incubation time-72 hr, temp-37 °C and 200 rpm; Efficiency-45%	[99]
Corynebacterium paurometabolum isolated from	Synthetic $K_2Cr_2O_7$ solution, 2 mM	Vogel Bonner broth in 100 ml Erlenmeyer flask; optimum condition:	[90]

chromite mine seepage		pH-7, temp.-35 ^{o}C, incubation time-8 days and 120 rpm; Efficiency-62.5%	
Alcaligenes faecalis and *Pseudochrobactrum saccharolyticum* isolated from contaminated Effluent	Synthetic $K_2Cr_2O_7$ solution, 10 and 100 mg/L; Industrial effluent, 10 mg/L	Luria Bertani culture medium in 300 mL bottle at 180 rpm; parameters: isolates comparison, temp., nutrient supplements and incubation time; Efficiency-100 % for both synthetic and effluent	[77]
Bacillus Cereus isolated from agricultural field, MIC-1450 mg/L	Synthetic $K_2Cr_2O_7$ solution,100 to 500 mg/L	100mL Luria Bertani broth in 250 ml Erlenmeyer flask; conditions: temp.-30 ^{o}C and incubation time 48 hr; Efficiency-70%	[106]
Anaerobic culture at anode and denitrifying anaerobic mixed cultures at cathode	Synthetic $K_2Cr_2O_7$ solution, up to 80 mg/L	Microbial fuel cell with each compartment volume-230 mL, electrode-graphite, Nutrient media [196]; Efficiency-70%	[175]
Mixture of mesophilic anaerobic digested sludge and aerobic activated sludge from WTP at a ratio of 1:1	Ground water, 1 to 30 mg/L; Cr(VI) conc. manage by adding $K_2Cr_2O_7$	Two SBR fed with groundwater of 3 L (total volume=5 L) with anaerobic and anoxic; conditions; design parameters: feeding time-0.5 hr, reaction time-22 hr, settling time-1 hr, decanting time-0.5 hr, sludge retention time-10 days and hydraulic residence time-1.7 days; Efficiency- 99% up to initial Cr(VI) conc. 10 mg/L	[167]
Desulfovibrio vulgaris strain isolated from subsurface	Ground water, 50 µM; Cr(VI) conc. manage by adding $K_2Cr_2O_7$	500 mL lactate–sulfate medium media in 1 L glass bottle modified to serum bottle; conditions: presence of hematite or Al-goethite or nontronite (NAu-2); Efficiency-100 % in hematite	[114]
Pseudomonas sp. isolated from industrial soil	Synthetic $K_2Cr_2O_7$ solution, up to 150 mg/L	Nutrient broth in 250 ml Erlenmeyer flask; conditions: pH- 6, initial Cr(VI) conc.-100 mg/L, incubation time-120 hr and temp. 28 ^{o}C; Efficiency-60 %	[83]
Bacillus subtilis isolated from tannery effluent contaminated	Synthetic $K_2Cr_2O_7$ solution, 50 mg/L	CA-M9 Minimal Media with 5% seed culture; conditions: pH-9, temp.-30 ^{o}C and 100 rpm; Efficiency-100 %	[105]

soil			
Sporosarcina saromensi isolated from intertidal zones at low tide	Synthetic $K_2Cr_2O_7$ solution, up to150 mg/L	216LB medium and 4% seed inoculums in Erlenmeyer flask, 200 rpm and 24 hr incubation; parameters: initial Cr(VI) concentration, pH and temperature; Efficiency-100 %	[100]
Chlorella vulgaris laboratory culture	Tannery wastewater, 3.22 mg/L	100 mL algal culture medium in 250 mL Erlenmeyer flask at temp. 28 °C under fluorescent lights 150-300 $\mu mol.m^{-2}. s^{-1}$ photons; Efficiency-100%	[143]
Penicillium commune, Paecilomyces lilacinus, Cladosporium perangustum, Cladosporium perangustum and *Fusarium equiseti* isolated from Soil, sludge and wastewater samples	Tannery wastewater, 9.86 mg/L	1 L bioreactor (12 cm in diameter and 20 cm in height) with modified minimal medium, glucose and ammonium nitrate supplemented, temp.-28 ^oC and pH-4; Efficiency-73 % in 12 hr	[75]
Aspergillus niger, A. flavus, A. *fumigatus*, *A. nidulans*, *A. heteromorphus*, *A. foetidus,* and *A. viridinutans* isolated from soil	Tannery wastewater, 290 mg/L	50 mL flask; optimum conditions: pH-3, fungi biomass-4g, initial Cr(VI) concentration-18 mg/L and strain *A. niger*; Efficiency-96.3 %	[128]
Laboratory culture *Arthrobacter viscosus*	Synthetic $K_2Cr_2O_7$ solution, 100 mg/L for batch and 25 mg/L for column	100 mL media in 250 mL Erlenmeyer flasks at 150 rpm; Parameters: pH, biomass conc., and contact time; star shaped column 17 mm external diameter and height of 10 mm, flow rate-10 mL/min up flow method for 120 hr and pH-2 at room temp.; Efficiency-100% (batch study) and in column equilibrium achieved in 450 min with Cr uptake 20.37 mg/g	[110]

Bacillus pumilus, Pseudomonas doudoroffii and *Exiguobacterium* isolated from tannery effluent	Synthetic K_2CrO_4solution, 100 to 1000 mg/L	DeLeo and Ehrlich medium; optimum conditions:150 rpm, temp.-37 ^oC, incubation time-24 hr, pH-7 and initial Cr(VI) concentration of 100 mg/L; Efficiency-82.4, 71.2 and 52.1 % by *B. pumilus, P. doudoroffii* and *Exiguobacterium*	[82]
Acinetobacter sp. isolated from aerator liquid of activated sludge process	Synthetic $K_2Cr_2O_7$ solution, 200 mg/L	100 mL LB media in Erlenmeyer flasks; conditions: temp.-37 ^oC, 150 rpm and initial Cr(VI)-200 mg/L; Efficiency-100 %	[94]
Pseudochrobactrum saccharolyticum isolated from chromium contaminated site	Synthetic $K_2Cr_2O_7$ solution, 55 to 360 mg/L	Modified Luria-Bertani media; optimum conditions: pH-8.3, initial Cr(VI) conc.-55 mg/L, NaCl-20 mg/L, and 1.47×10^9 cells/mL; Efficiency-100 % in 96 hr	[85]
Anaerobic methane oxidizing archaea from activated sludge of a WTP	Synthetic $K_2Cr_2O_7$ solution, 0.01 mM	3 L laboratory glass reactor with 2 L Mineral salt media sparged with N_2-CO_2 at 35 ^oC and pH between 7.0 and 8.5; Efficiency-100%	[169]
A. flavus isolated from contaminated soil sample	Synthetic $K_2Cr_2O_7$ solution, 10 to 60 mg/L	50 ml of nutrient broth medium in 250 ml screw capped Erlenmeyer flasks incubated at 120 rpm and 30 ^oC; parameters: initial metal ions concentration and incubation period and pH; Efficiency-71 %	[129]
Trichoderma asperellum isolated from contaminated site of non-ferrous metal mine	Synthetic $K_2Cr_2O_7$ solution, 10 mg/L	200 mL liquid medium at temp. 28 ^oC, 150 rpm, pH-6.8 to 7.27 and incubation time-96 hr; Efficiency-100 %	[184]
Leucobacter komagatae and *Leucobacter albus* isolated from contaminated soil of tannery factory	Synthetic $K_2Cr_2O_7$ solution, 400 mg/L	100 ml Luria–Bertani medium in Erlenmeyer flasks at temp.-35 °C and 160 rpm; conditions: aerobic, facultative anaerobic (without shaking), and strict anaerobic; Efficiency-100 % for facultative anaerobic, 33.3 % for aerobic and 65.4 % strict anaerobic Incubation in 96 hr	[185]

Anaerobic activated sludge as inoculums, Gamma-proteobacteria found in post operation study	Synthetic $K_2Cr_2O_7$ solution, 20 mg/L	Dual-chamber MFC, volume-70 mL, gastight, separated by proton exchange membrane, Graphite sheet as electrodes; Efficiency-79 % ex-situ and 20 % in-situ	[177]
Stock culture *Pseudomonas mendocina,* MIC-25 mg/L	Synthetic $K_2Cr_2O_7$ solution, 10 to 25 mg/L	100mL triptic soy broth in 250 mL flasks incubated at 37 ^oC and 125 rpm; optimum conditions: pH-6, initial Cr(VI) concentration-10 mg/L, incubation time -24 hr and galactronic acid; Efficiency-100 %	[81]
Acenetobacter calcoaciticus isolated from mining area, MIC-1000 mg/L	Synthetic $K_2Cr_2O_7$ solution, 100 mg/L	100 mL Luria Bertani broth media in 250 mL Erlenmeyer flasks; optimum conditions: pH-8, temp.-30 ^oC, incubation time-24hr and 100rpm; Efficiency- 89 %	[186]
Plant species *Phragmites australis, Salix viminalis* and *Ailanthus altissima*	Synthetic $Na_2Cr_2O_7$ solution, 10 m/L	Phytoremediation; 2 L pots filled with clay soil irrigated continuously with flow rate of 0.2 L/min, using a peristaltic pump for 360 days; Efficiency-56 % with *Phragmites*, 70 % with *Salix*	[135]
Arthrobacter isolated from chromite mine overburden	Chromite mine effluents, 60 µM	Cell-free chromate reductase enzyme; conditions:120 rpm, pH-6.5 to 7.5 and temperature 35^oC; Efficiency-> 75% with NADH	[108]
Nesterenkonia sp. isolated from effluents of tanneries, MIC-600 mM	Synthetic $K_2Cr_2O_7$ solution, 0.2 mM	25 mL of Nutrient broth medium in100 mL Erlenmeyer flasks; conditions: incubation time-24 hr, temp.-35 ^oC and 100 rpm; Efficiency-100 %	[187]
Halomonas genus isolated from Soap Lake	Synthetic $K_2Cr_2O_7$ solution, 0.1 mM	100 mL Modified Soap Lake Basal Media in 150 mL serum bottles; conditions: pH-9, 130 rpm and temp-35 ^oC; Efficiency-80% in 25 days	[188]

Stenorophomonas maltophilia isolated from feather disposal site grown in Feather meal broth	Synthetic $K_2Cr_2O_7$ solution, 50 and 100 mg/L	Feather protein hydrolysate used for reduction 50 ml of peptone water at temp-35 ^oC and 125 rpm for 1 hr; Efficiency-78 %	[93]
Bacillus cereus isolated from soil sample	Tannery effluent, total chromium 2.4 mg/L	100 mL of sterilized tannery effluent including 10 mL inoculums in 250 mL Erlenmeyer flasks; conditions: temp.-35 ^oC and 120 rpm for 48 hr; Efficiency-92% (immobilized cells) and 73% (free cell)	[107]
Pseudomonas genus Isolated from circulating cooling system of iron and steel plant, MIC-6.5 mmol/L	Synthetic K_2CrO_4 solution, 0.5 to 3 mmol/L	100 mL LB media in 250 mL Erlenmeyer flask; optimum conditions: pH-7 to 9, initial Cr(VI) concentration-3 mmol/L, and inoculating dose-10 %(v/v) for both growing cells and free cells; Efficiency- 100 %	[189]
Acinetobacter isolated from tanneries effluents	Synthetic $K_2Cr_2O_7$ solution, 50 to 200 mg/L	NB medium; conditions: pH-10, temperature 30 ^oC, and exposure time-72 hr and initial Cr(VI) concentration-50 mg/L; Efficiency- 100 %	[190]
Anaerobic sludge collected from the anaerobic digester of the sewage treatment plant	Synthetic $K_2Cr_2O_7$ solution, 75 to 300 mg/L	A two-chambered reactor, dimension (8 cm diameter and 10 cm length; 500 mL capacity and 250 mL working volume), separated by proton exchange membrane (Nafion 117), plain carbon cloth as electrode; Efficiency-100 % at pH-2, 300 mg/L, 150 mg/L and 75 mg/L required 1350 min, 750 min and 180 min, respectively	[174]
Staphylococcus arlettae strain isolated from tannery effluent, MIC-2000 mg/L in liquid and 5000 mg/L in solid media	Synthetic $K_2Cr_2O_7$ solution, 500 and 1000 mg/L	Petri dishes containing tryptone soya peptone (TS) media incubated at 37 oC and 120 rpm; Efficiency-98% and 75% for initial Cr(VI) concentrations of 500 and 1000 mg/L, respectively in 120 hr	[88]

Bacilli sp. isolated from tannery effluent	Synthetic $K_2Cr_2O_7$ solution, 21.5, 43 and 80.63 mg/L	50 mL of Luria-Bertani media in 250 mL Erlenmeyer flasks; Efficiency-87% for initial Cr(VI) conc. 21.5 mg/L in 72 hr	[191]
Acinetobacter haemolyticus isolated from textile effluent	Synthetic $K_2Cr_2O_7$ solution, 10 to 100 mg/L	100mL NB medium in 250mL Erlenmeyer flasks incubated at 30 ºC and 200 rpm for 48 hr; Efficiency- >90 %	[95]
Arthrobacter sp. and *Pseudomonas* sp. isolated from chromite overburden	Synthetic $K_2Cr_2O_7$ solution, 2 mM	20 mL Vogel Bonner (VB) broth and modified KSC medium at pH-7 in 100 mL Erlenmeyer flask incubated at 35 °C and 120 rpm; Efficiency-50% in VB broth and 80% KSC medium	[192]
Ochrobactrum intermedium isolated from tannery effluent	Synthetic K_2CrO_4 Solution, 100, 500 and 1000 µg/ml; Industrial sewage water sample, Cr(VI)-150 µg/ml, Fe-101 µg/ml, Cu-75 µg/ml, Zn-8 µg/ml, Ni-114 µg/ml, Co-4 µg/ml, Pb < 1 µg/ml	DeLeo and Ehrlich (DE) medium of pH-7 incubated at 37 oC and 150 rpm; Efficiency- 97.1%, 95.5% and 91.2% with initial Cr(VI) concentrations 150, 500 and 1000 µg/ml, respectively, in 72 hr for industrial sewage water sample; 87%, 83% and 65% with initial Cr(VI) concentrations 150, 500 and 1000 µg/ml, respectively, in 72 hr for artificial sewage water sample	[193]
Lab culture *Cellulomonas* species isolated from contaminated soil preserved in tryptic soy broth	Synthetic K_2CrO_4 Solution, 7 mg/L	30-mL anaerobic culture tubes sealed with butyl rubber stoppers and aluminum crimp seals, sucrose supplement as carbon, electron shuttles anthraquinone-2,6-disulfonate AQDS and Fe(III); Efficiency-100 % in 25 hr in sucrose+AQDS, >90% in 8 hr in sucrose+AQDS+hematite	[101]
Halomonas sp. isolated from tannery effluent	Synthetic K_2CrO_4 Solution, 50 mg/ L	25 mL of Luria Bertani medium in 100 mL Erlenmeyer flasks at pH from 6 to 11, incubated at 30 ºC and 120 rpm; Efficiency- 82 % in 48 hr	[87]

Lab culture *Escherichia coli* basal medium	Synthetic $K_2Cr_2O_7$ solution, 10mg/L	250 ml serum bottles with butyl rubber stoppers, Glucose as carbon source, and 40 mg/L Fe(III) dosage, incubated at 32°C and 150 rpm; Efficiency-95 %	[102]
Bacillus sp. isolated from soil samples of land farming site	Synthetic $K_2Cr_2O_7$ solution, 2 to 8 mg/L	Bioreactor columns of 60 ml sterile polypropylene syringes (2.5 cm internal diameter and 13.5 cm length) packed with 45mL Celite, Amberlite and Ca-Alginate in separate columns, flow rate-3, 6, 10, and 14 mL/hr corresponding to retention times of 15, 7.5, 4.5 and 3.2, respectively; Efficiency-98% with cell-free extracts and 84% with immobilized intact cells for initial Cr(VI) conc. 2 to 8 mg/L at flow rates 3 to 6 mL/h with immobilizers Celite and Ca-Alginate	[103]
Lab culture *Bacillus sphaericus* in Tryptic Soy Agar	Synthetic $K_2Cr_2O_7$ solution, 10 to 50 μM	10 mL of mineral salts broth supplemented with 0.1 % glucose in 100 mL of Erlenmeyer flask incubated at 32 °C and 120 rpm with immobilizers: Polyvinyl alginate, polyvinyl borate, calcium alginate, agarose and agar-agar; Efficiency-95% in 24 hr	[194]
Planococcus maritimus isolated from a coastal region, MIC-500 mg/L	Synthetic $K_2Cr_2O_7$ solution, 100 to 500 mg/L	100 mL Luria Bertani medium in 250 mL Erlenmeyer flask; optimum conditions: pH-7, temp.-35 °C, 140 rpm and 4% NaCl; Efficiency-100% with initial Cr(VI) conc. 100 and 200 mg/L within 24 and 28 hr, respectively	[195]
Providencia sp. isolated from contaminated sites of chemical industries, MIC-1000 mg/L	Synthetic $K_2Cr_2O_7$ solution, 100 to 400 mg/L	Luria Bertani medium; Efficiency-100% with initial Cr(VI) conc. ranging from 100 to 300 mg/L and 99 % with initial Cr(VI) conc. 400 mg/L, at pH-7 and temperature 37 ºC	[197]
Halomonas aquamarina Sp. isolated from Cr(VI)-polluted	Synthetic $K_2Cr_2O_7$ solution, 0.2 to 3.0 mM	100 ml of YEPG-NaCl broth culture medium, cell free extract, pH-6.5 and temperature- 28 oC, NADH supplement, 80 g/L NaCl; Efficiency-81.5% in 24 hr	[86]

sediments, MIC-4 mM			
Sulfate reducing sludge from an anaerobic baffled reactor treating acid mine drainage	Synthetic $K_2Cr_2O_7$ solution, 5 to 50 mg/L	500 mL glass column bioreactor filled with elemental sulfur, flow rate-500 to 1400 mL/day, HRT-0.36 to 1 day, 56 mg/L KH_2PO_4, 110 mg/L NH_4Cl, 11 mg/L ascorbic acid and 50 mg/L yeast extract and 1000 mg/L ethanol/acetate as electron donor carbon source or COD; Efficiency-97%	[198]
Phytoremediation by *Halimione Portulacoides* grown in Hoagland nutrient solution	Synthetic $K_2Cr_2O_7$ solution, 15 and 30mg/L	Greenhouse at temperature 25 ^oC; Efficiency->75 %	[137]
Pannonibacter phragmitetus isolated from chromium containing slag	Synthetic $K_2Cr_2O_7$ solution, 200 mg/L	20 mL media in 40 mL sealed serum bottles; parameters: carbon sources as lactose, fructose, glucose, pyruvate, citrate, formate, lactate, NADPH and NADH at pH-10 and 35 ^oC; Efficiency-100% in 24 hr	[199]
Rhodococcus erythopolis isolated from coal mine area	Synthetic $K_2Cr_2O_7$ solution, 1 to 100 mg/L	Optimum conditions: pH-5 to 7, temperature-20 to 35 ^oC; Efficiency-89%	[200]
Geobacter metallireducens, *Desulfovibrio desulfuricans* and *Sulfurospirillum barnesii*	Synthetic K_2CrO_4 Solution, 25 to 100 mM	20 mL of culture in 25 mL serum bottle, *G. metallireducens* grown on freshwater acetate medium with nitrate, *D. desulfuricans* and *S.barnesii* grown on SES3 freshwater medium with lactate and nitrate; Efficiency-72 % by *D. desulfuricans*, and *S. barnesii*	[201]
Pseudomonas aeruginosa isolated from soil samples collected hydrocarbon contaminated sites	Effluent of hard chrome plating industry, 2100 mg/L	5 L reactor inoculated with 50 ml, hydraulic retention time-24 hr, inoculum size-10% *v/v* (108 cells/mL), pH-7, temperature-32 ^oC, and flow rate-2.5 mL/min; Efficiency-84.85%	[202]

Arthrobacter sp. isolated from metalliferous mine overburden	Synthetic Cr(VI), 2 mM	20 mL Vogel Bonner broth in 100 mL Erlenmeyer flask, pH-7, temp.-35 ^{o}C, 120 rpm; Effect of electron donors as propionate, acetate, benzoate, glucose, sucrose, glycerol, propylene glycol, chlorophenol and cresol; Efficiency-100% with glycerol in 4 days	[67]
Arthrobacter sp. isolated from creosote polluted site, MIC-850 mg/L	Synthetic $K_2Cr_2O_7$ solution, 100 mg/L	100 mL M9 media in 250 mL Erlenmeyer flask; optimum conditions: initial Cr(VI) conc.-45 mg/L, temp-30 ^{o}C, pH-8, 150 rpm and 10 g/L glucose; Efficiency-100%	[203]
Pannonibacter phragmitetus isolated from sludge of chromate factory, MIC-1000 mg/L	Synthetic $K_2Cr_2O_7$ solution,100 to 1000 mg/L	100 mL Luria Bertani medium in 250 mL Erlenmeyer flasks; optimum conditions: initial Cr(VI) conc.-300 mg/L, temp.-37 ^{o}C, 150 rpm and pH-9; Efficiency-100%	[204]
Bacillus amyloliquefaciens isolated from chromite mine soil samples, MIC-500 mg/L	Synthetic $K_2Cr_2O_7$ solution, 100 mg/L	100 mL nutrient media in 250 mL Erlenmeyer flask, pH-7, incubation time 24 hr, temp-35 $^{\circ}$C and 100 rpm; Efficiency-100%	[205]
Lab culture *Pseudomonas mendocina*	Synthetic $K_2Cr_2O_7$ solution, up to 25 mg/L	100 mL tryptic soy broth in 250 mL Erlenmeyer flasks in presence of Cu(II), Fe(II), Ba(II) and Ni(II); Efficiency-100 % in 36 hr in presence of Cu(II)	[206]
Streptomyces violaceoruber isolated from wastewater discharging Yellow River	Synthetic $K_2Cr_2O_7$ solution, 0.6 mM	In Starch-Casein agar (SC) medium, optimum temperature-28 ^{o}C and pH-7; Efficiency-92.86% in 144 hr	[207]
Halomonas genus isolated from Mono Lake	Synthetic K_2CrO_4 Solution, 2.5 mM	15 mL Basal medium in 20 mL serum bottles at pH-10 and temp-30 °C; Efficiency-100 %	[208]

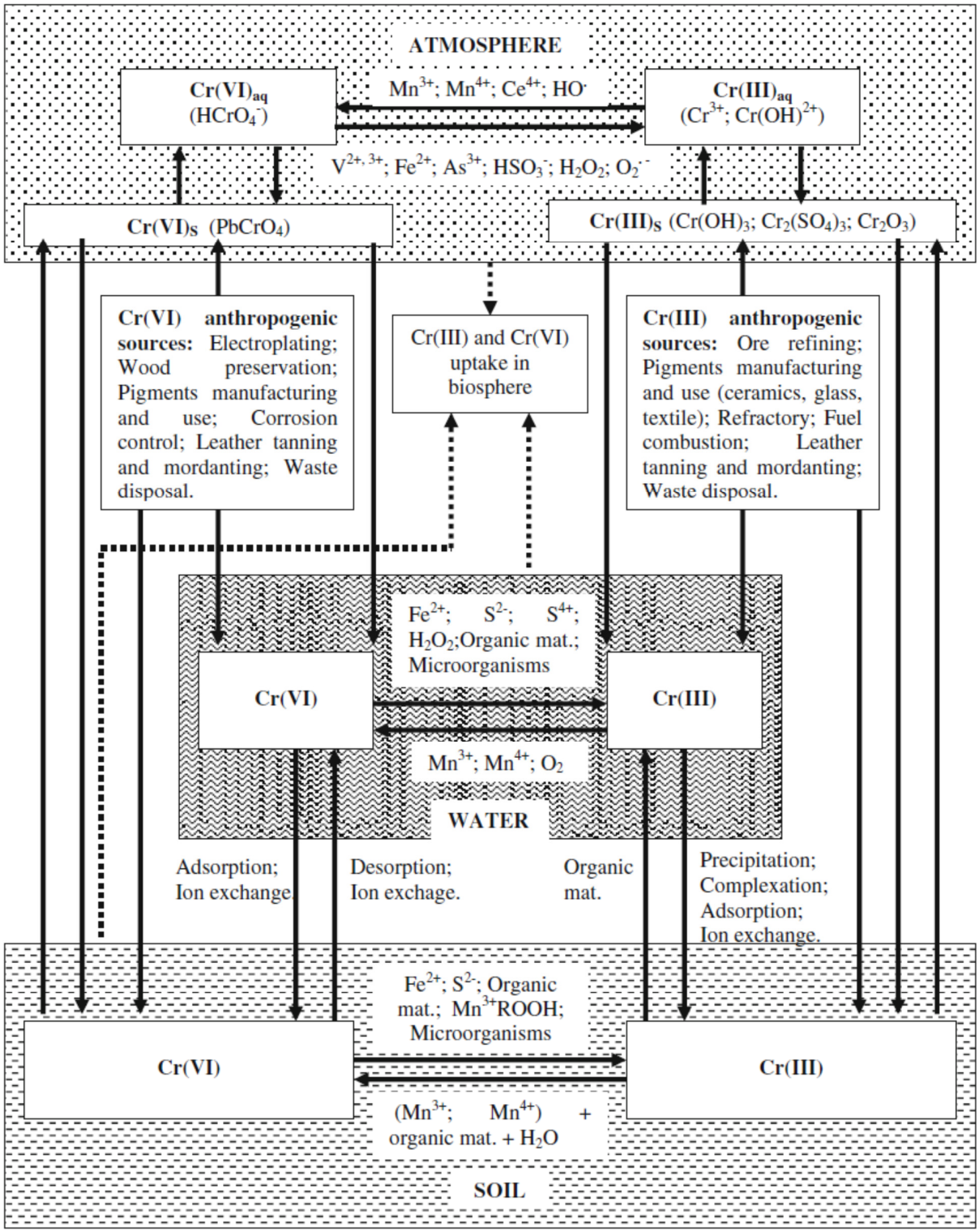

Figure 1. Biogeochemical cycle of Chromium in biosphere. [7]

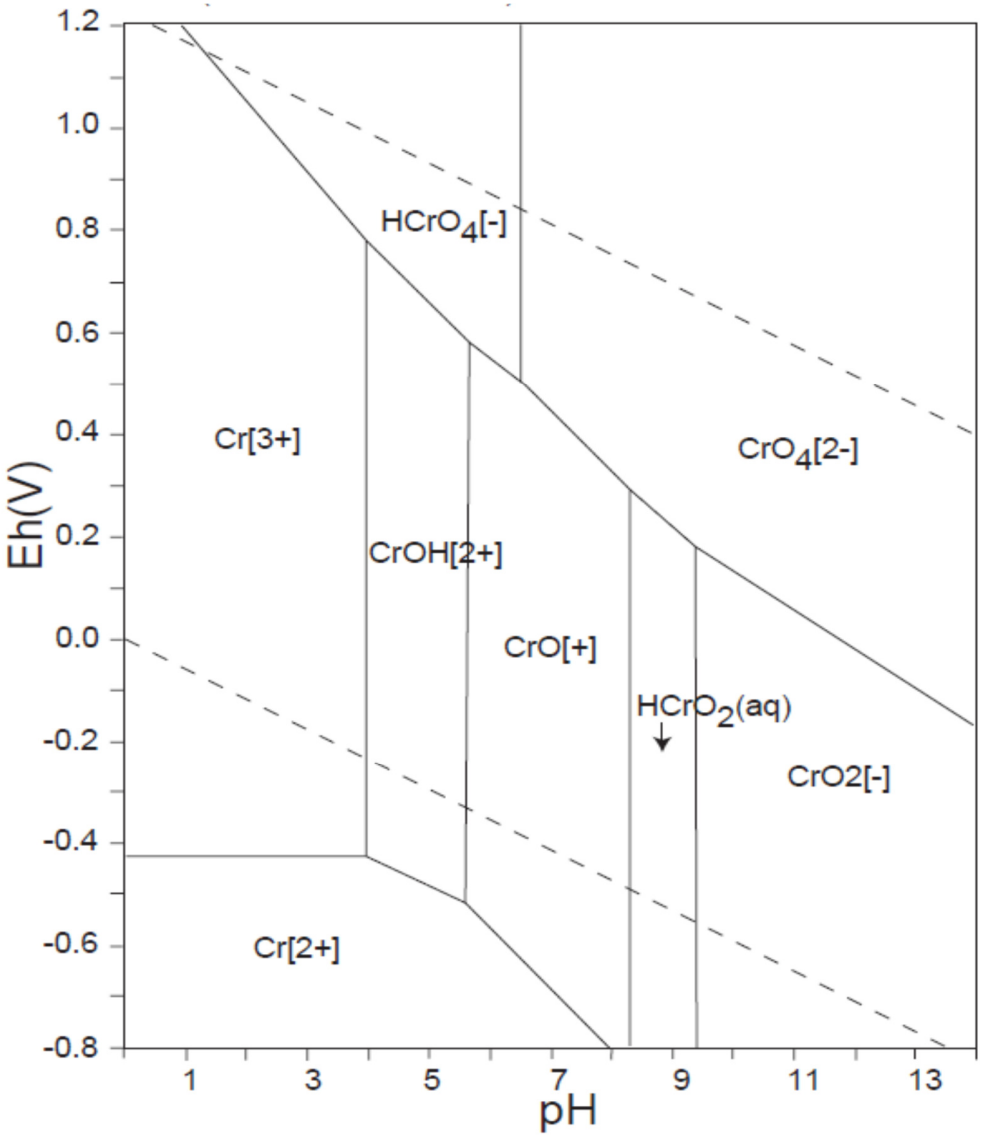

Figure 2. Eh-pH phase diagram for chromium. [183]

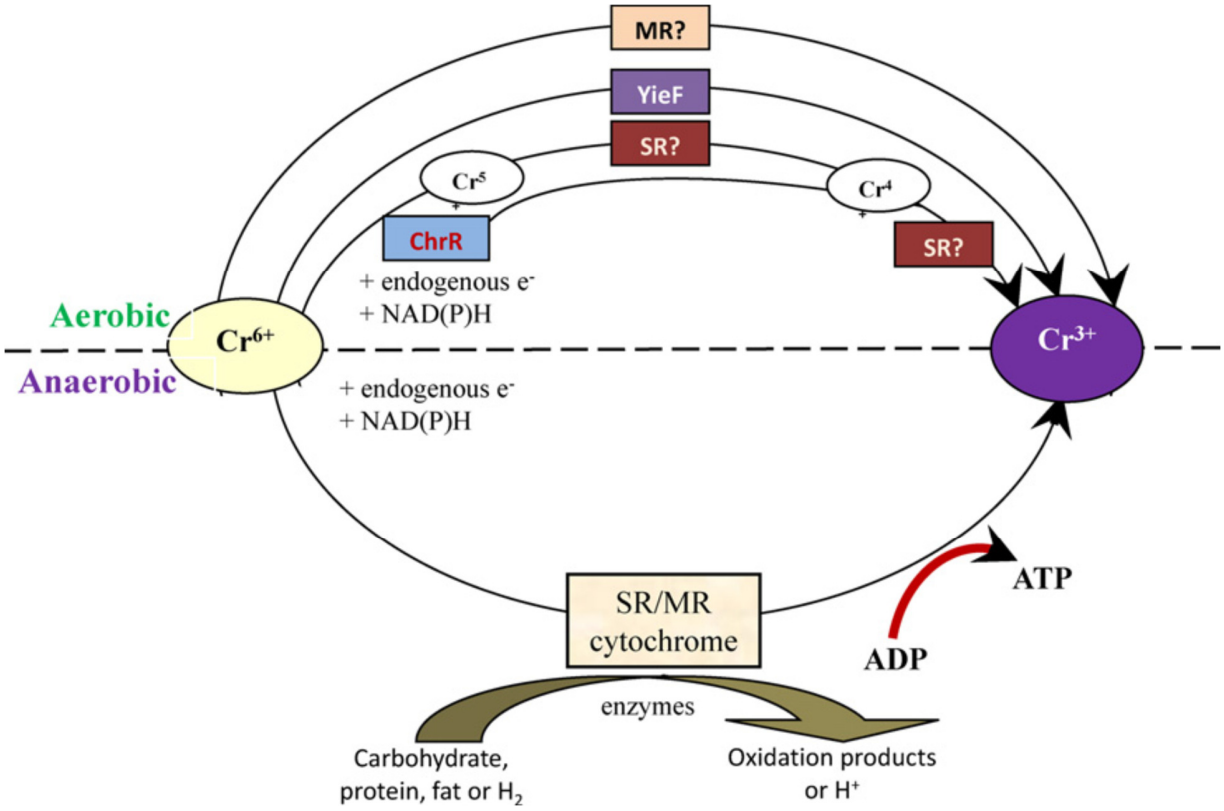

Figure 3. Mechanism of Cr(VI) reduction in aerobic and anaerobic conditions. [10]

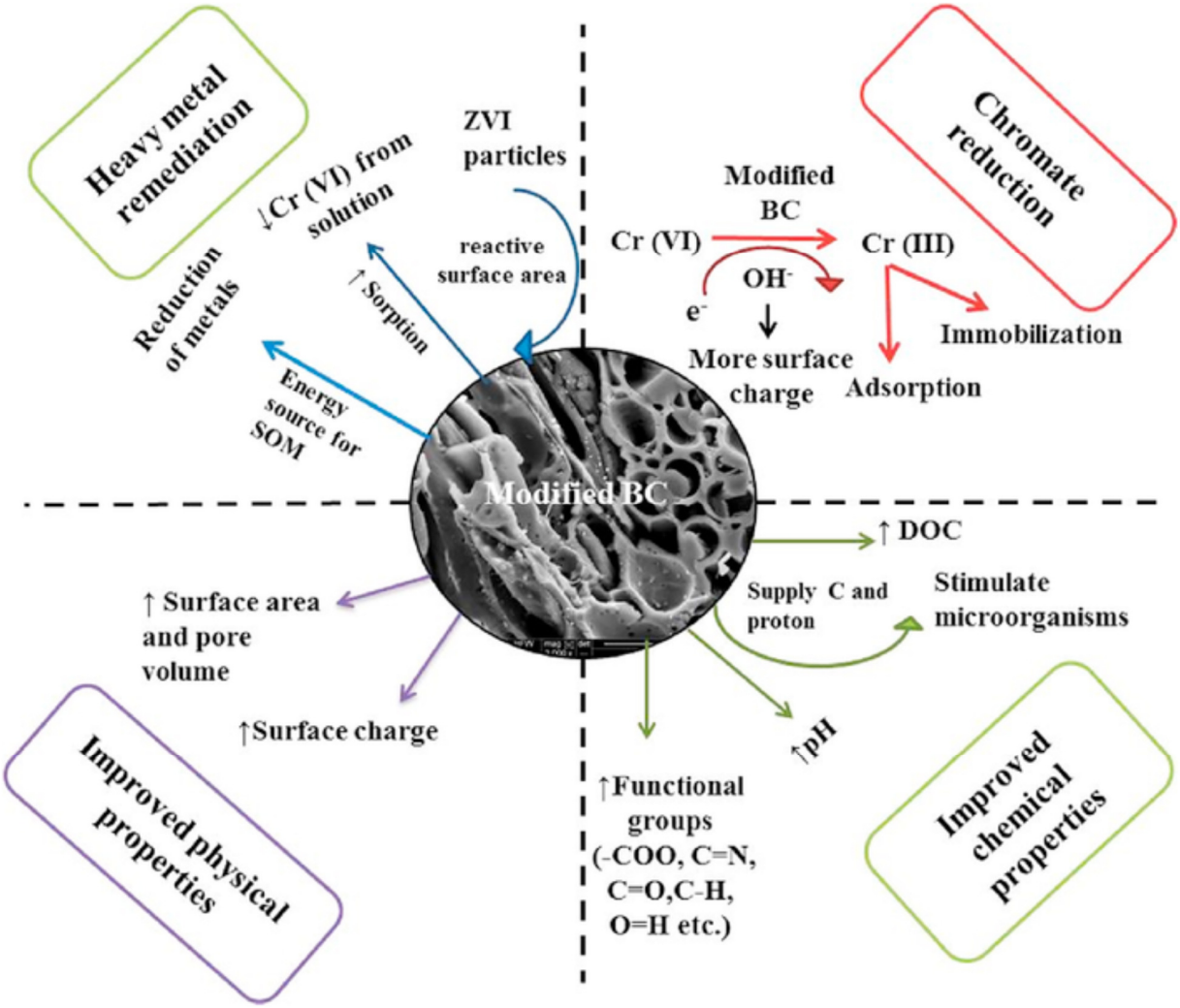

Figure 4. Cr(VI) reduction by the surface modified biochars proposed by Mandal et al.[162]

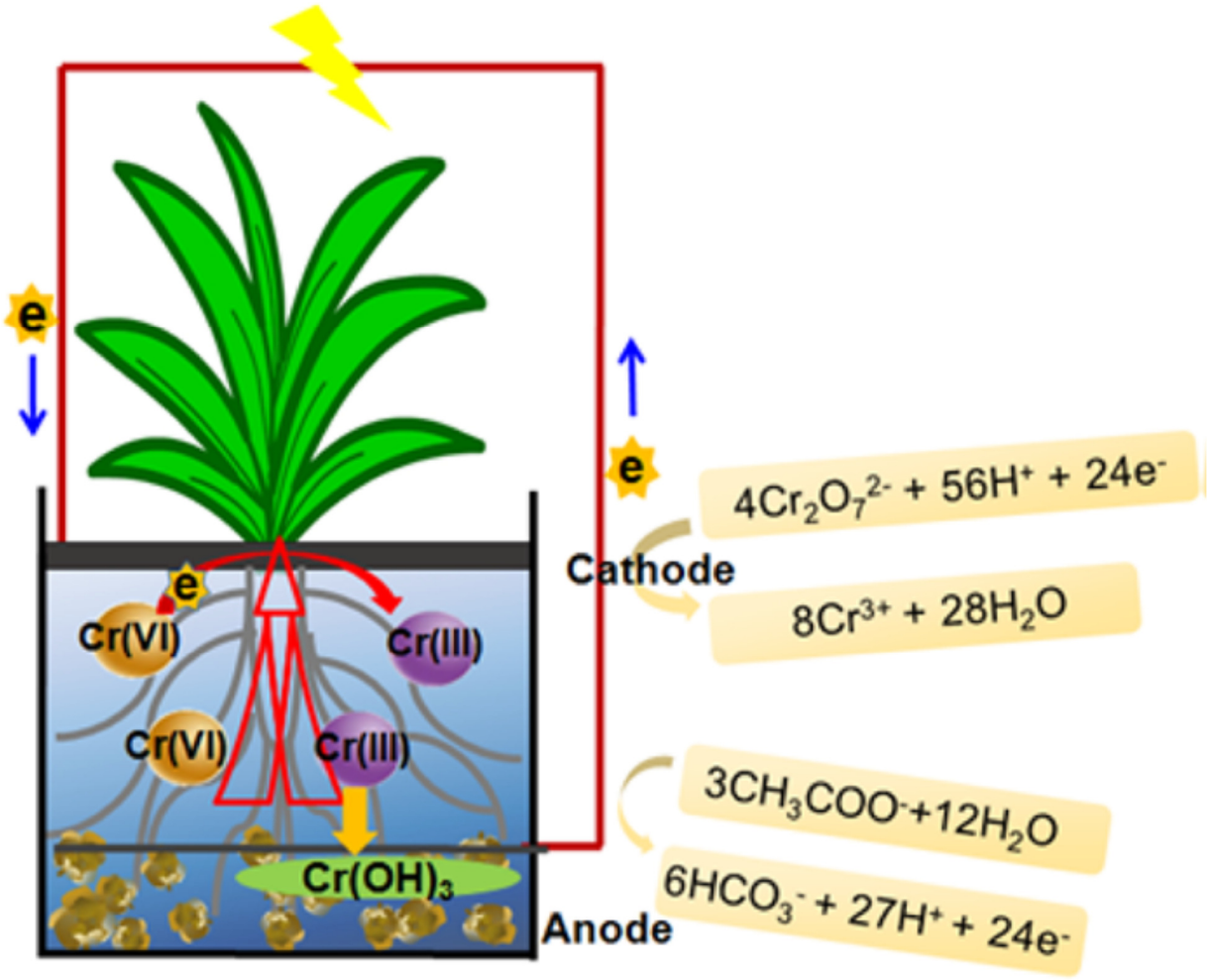

Figure 5. Schematic diagram of Ryegrass (*Lolium perenne*) plant-microbial fuel cell. [179]